

Hypothesis

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[Chika Edward Uzoigwe](#)*

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Hypothesis

Unconventional Superconductors Explained – Adiabatic Delocalised Shared Electron Transfer

Chika Edward Uzoigwe

Independent Researcher; Harcourt House, Sheffield, UK; chika@doctors.org.uk

Abstract

Superconductivity is a Delphic quantum phenomenon whereby certain materials, below a critical transition temperature, remarkably exhibit no electrical resistance. It remains imperfectly understood. The Bardeen-Cooper-Schreifer (BCS) theory, characterised by travelling electron Cooper pairs, explains the function of *conventional* superconductors but not that of *unconventional* superconductors, which continue to pose a conundrum. Neither can BCS account for Type II superconductivity whereby a sufficiently strong magnetic field can penetrate a superconductor, creating circuitry cyclones or vortices. Further the origins of High Temperature superconduction remain unelucidated; being beyond the explicative apses of BCS. Herein these outstanding phenomena are explained. It is posited that unconventional superconductivity is contingent upon delocalised electrons. There is “*electron dysphoria*”, where there is no clear atomic electron ownership, neither is there a definitive point where one electron ends and the second begins. This is analogous to the electron “*nebula*” of the benzene 6 carbon ring, where classically there are 3 single and 3 double bonds. However on measurement all bonds are of equal length. All carbons share all π electrons equally in a plane above the carbon ring. Thus unconventional superconductivity operates via Shared Adiabatic Delocalised Shared Electron Transfer (ADSET). This condensate supplants the Cooper pair paradigm. This also accounts for high dielectric constant, indicative of high polarisability, of unconventional organic and cuprate superconductors. We discuss the quantum syphon paradigm for the initiation of current. To achieve unconventional superconduction a laminar structure is often required, with delocalised electrons in the plain above or in-between lamina. This is observed in the cuprates and nickelates. Also organo-metallic superconductors have been described which are critically contingent upon the benzene motif for function. This lamina bauplan accounts for anisotropy observed in this mode of superconduction. Superconductivity is only observed in the plain parallel to the delocalised electrons. Further given that many already exist in a state of electron delocalisation at ambient temperatures, superconductive phenomena can be achieved at higher temperatures compared to conventional superconductors. This explains the pre-eminence of unconventional superconduction amongst high-temperature superconduction. In addition, the tessellating polyhedral units, that create the planar structures, account for the partial penetration of magnetic fields seen with the latter. In such instances the current circulates around each structural unit as it would in a single benzene ring. An examination of the gamut of materials exhibiting Type II superconduction points to the possibility that unconventional and conductional superconductors may not be mutually exclusive. Some may exhibit both modes of superconductivity dependent upon the milieu and anisotropy. A similar formula may account for the superconductivity of twisted bilayer Graphene. Graphene comprises a carbon mono-layer laminated between delocalised π orbital of electrons. Twisting creates a variegated probability cloud thus potentially mimicking a Daedalian Thouless pump that effect adiabatic church transfer. Tellingly twisting parallel sheets of graphene creates a quantised charge. This also accounts for the behaviours of Strange metals in particular their characteristic ability display of linear increases in resistivity with increasing temperature above the critical temperature. The quadratic relationship seen in Normal metals is attributed to electron-electron scattering. Given this does not and cannot occur with delocalised electrons only a linear relationship is observed in metals exploiting delocalised electron migration in conduction. Within our unconventional superconduction paradigm an electron cannot be said to move but rather already

exists in the putative space that the potential difference takes it. Nature may have exploited this principle in energy generation by chemiosmosis. Classically this process relies upon the serendipitous encounter of a few rare protons with ATP synthase enzyme, secluded in crypts of subcellular mitochondria. However, protons in water, due to hydrogen bonding and the Nuclear Quantum Effects of the diminutive proton, can be delocalised. Hence the distinction between hydrogen ion and hydrogen atom of water molecule is blurred. Thus proton does not move from one location to the next but is already juxtaposed to the ATP synthase molecule, in the guise of the water hydrogen atom in closest proximity to enzyme. Hence nature exploits 307K, body temperature, superconductivity while we, in the scientific community, continue to muse on the mechanism of 77K unconventional superconduction and entertain oneiric fantasies of room temperature superconduction. However this epiphany, described herein, promises the real prospect of room temperature superconduction.

Keywords: conventional superconductors; unconventional superconductors; delocalised electrons; benzene; adiabatic delocalised shared electron transfer; ADSET; Meissner effect; twisted bilayer graphene; twistrionics; thoulless pump; water; nuclear quantum effects

1. Introduction

The current eponymous Bardeen-Cooper-Schreifer (BCS) model of superconductivity is contingent upon Cooper pairs; with electrons segueing from fermion pair to boson unity. However this characterisation does not apply to *unconventional* superconductors, a class to which all known, so called *high temperature* superconductors belong [1]. Here we posit that unconventional and thus high temperature superconductors depend rather on adiabatic electron transfer. This is in some ways a chimeric quantum and classical phenomenon. Electrons are delocalised and perfectly shared between nuclei as they transit. No energy is required to break one electron nuclear attraction to migrate to the next. In normal “non-super” conduction there is energy liberated on formation of the new electron nuclear bond. Nonetheless there remains an energy threshold to overcome to transit escape the orbit of one nucleus. The electrons therefore nestle in an energy nadir between two peaks (Figure 1). In unconventional superconductivity we submit there is only an energy trough with no peaks. Consider the motion of electrons in the benzene ring in the π electron cloud, where all the electrons are shared equally by the carbons of the ring.

A similar pattern has been observed in an unexpected guise namely the proton in water during a mode of the Grotthuss mechanism of en masse proton hopping in combination with Nuclear Quantum Effects (NQE). At most pHs protons are in the minority. However due to hydrogen bonding and NQE the proton is delocalised. One cannot discriminate which is the proton and which is the hydrogen bonded hydrogen atom of water. Here adiabatic transfer occurs when the proton is perfectly shared between oxygen of protons in what is termed the short Zundel configuration of protonated water [2]. This exploitation of the proton superconductivity illuminates the mechanism of unconventional superconduction.

2. Conventional Low Temperature Superconduction

Conventional superconduction occurs below a transition temperature. Here the atomic and molecular excursions due to thermodynamic energy are reduced to a critical value. Electron flow is unimpeded by impact with contiguous atoms and molecules. The egress of one electron is followed by a focus of positive charge which attracts a second electron but also reverberates in composite lattice. Electrons therefore travel as Cooper pairs. This is the seminal Bardeen-Cooper-Schreifer (BCS) theory [3]. However Cooper pairs have not been reported in the context of unconventional class superconductor.

3. The Mystery: Aromatic Answers

Unconventional superconductors act in a different manner. The means of zero resistance electron mobilisation remains a mystery and is not mediated by Cooper pairs. They still exhibit a transition temperature. However this can be higher than that of conventional superconductors. Indeed so called *high-temperature* superconductors, thus far, have all tended to be operative via unconventional superconduction. These exhibit superconductivity at temperature above 77K [4].

Here we postulate that unconventional superconductors act by the flow of delocalised and shared electrons. As the temperature reduces, molecular and electron excursions diminish in amplitude. The net result is that electrons are perfectly shared in a quantum delocalised state. The “movement” from one location to the next is adiabatic. There is electron euphoria, where electrons are shared and not owned in a paragon delocalisation. No energy barrier must be overcome to move from one molecule to the next and energy is depleted by percussion with interposed molecules. The concept of electron “movement” in this conduction paradigm is somewhat contrived as there can be no determination where one electron terminates and the next begins. There is adiabatic, shared delocalised electron transfer (ASDET)

The most analogous phenomenon is the delocalised electrons of the benzene ring. Benzene consists of six carbons in ring, with each carbon attached to another carbon and a hydrogen species. Under a classical paradigm between the carbons there should three double bonds and three single bonds. However on measurement all the bonds are the same length. Hence π electrons are shared equally between all three carbons (Figure 2). There is “electron euphoria” with no clear ownership nor singularity where one electron ends and the second begins [5]. As there is perfect sharing, no energy is required to move from carbon to the next, indeed such a notion has no meaning. As a proof of concept the metallo-organic superconductors have been identified with the benzene ring being germane and indispensable to superconductivity [6]. Superconductivity has also been observed with aromatic (benzene containing) hydrocarbons [7]. Further they exhibit features consistent with unconventional superconductors.

The benzene ring typifies the structure of unconventional semiconductors. They are classically laminar between each plane is a nebula of delocalised “shared” electrons. During superconduction electrons do not flow *per se* but already occupy the location the any potential would place them. The concept is counterintuitive but is quantum and will be apparent when we discuss water. The paragon example is the cuprates and more recently the nickelates [8,9]. Cuprates are characterised by CuO₂ laminae with alternating interposed Yttrium and Barium, with two Barium atoms per Yttrium. Each oxygen binds two coppers, and each copper 4 oxygen molecules. There exists a delocalised electron π cloud between the CuO₂ laminae [10]. This we submit carries the zero-resistance current (Figure 3). Here it has been shown that by increasing the polyhedral layers.

Extrapolating from this principle one would anticipate superconductivity in graphite. Graphite is an allotrope, of carbon where each carbon is attached to three other carbons via sigma bonds, above this mesh is again a nebula of delocalised electrons in π bonds. As anticipated certain forms of graphite have exhibited superconductivity, telling *highly oriented pyrolytic graphite* (HOPG) has been reported to show superconductivity, even at room temperatures [11]. HOPG can be distinguished from basic graphite on two grounds. Firstly, as the name suggests, crystals are well-aligned with each other, thus maximising electron sharing and electron cloud overlap with no excursions from superior planes Secondly pyrolysis refers to the fact that between carbon laminae there are vertical bonds. Inter-laminar bonds maintain the highly orientated configuration. Without these vertical scaffolds, laminae are maintained in a fine equilibrium by van der Waal’s attraction and like-charge repulsion. However this tenuous separation can sterically and mechanically impede superconduction. Indeed voltage potentials may be applied non-parallel to the delocalised electrons, propelling them to the lamina and indeed pushing clouds to sufficient proximity to nuclei that they be captured by their attractive, thus compromising delocalisation. These observations point to the possibility that the other elements in unconventional superconductors such as the cuprates, including

Yttrium and Barium, may serve to maintain the integrity of the inter-laminar distance conducive to super conductivity

3.1. Accounting for Anisotropy

Our model explains a number of the properties of unconventional superconductors. The first is anisotropy [12], whereby superconductivity is only demonstrable in one plain or is directionally dependant. This is observed in cuprates, nickelates and graphite. This can clearly be explained by laminar nature of unconventional superconductors. Parallel to the plane of the electron nebula superconductivity subsists, orthogonal to it it does not and indeed it is impeded.

3.2. Meissner Effect Affirmation

All superconductors resist a magnetic field penetration. The approximation of a magnet generates a current equal and opposite the magnet provocateur which it repels. The strength of the magnet that can be overcome depends on the temperature. The closer this is to the transition temperature the weaker the repellable force. However type II superconductors exhibit a peculiar property whereby even below threshold magnet field strengths there exists another threshold at which the ambient magnetic field penetrates the superconductor and creates vortices, circulating around the field (Figures 4 and 5). This is inexplicable in the Cooper pair paradigm but axiomatic within the current model. The vortex is generated by the current circulating within each repeating structural unit or potentially several units of each lamina. Consider the case of benzene ring as a fundamental unit, delocalised electrons will circulate above and below the carbon ring when exposed to a magnet of sufficient strength. That is akin to each vortex observed in superconducting vortices of Type II superconductors. Significantly the recent organometallic with critical benzene rings as anticipated are Type II superconductors. Consistent with our hypothesis pyrolytic graphite is a Type II superconductor.

In support of this postulate Saipuddin et al produce a list of Type I superconductors of which all 26 were conventional [13]. Tellingly no Type I superconductors were unconventional superconductors. Their list of Type II superconductors comprised 18 unconventional superconductors but only 3 conventional superconductors namely Vanadium, Technetium and Niobium. The ability of these three "classical" conventional superconductors to act as Type II superconductors is fascinating and intriguing. It suggests that conventional and unconventional superconductivity may not exist as a mutually exclusive dichotomy. Materials may exhibit both properties contingent upon ambient conditions, notably temperature or even upon the plane of orientation of the driving potential difference. Niobium, Vanadium and Technetium all have crystalline structures. However completely incongruous with this structure, they have all been shown to uniquely exhibit marked anisotropy with regard to their superconductivity [14–16]; whereby properties are dependent upon direction an effector is applied which is hitherto explained. Hence we submit here that in certain orientations Niobium Vanadium and Technetium exploit unconventional superconductivity via the mechanism we propose, effected by plane of delocalised electrons. In the orthogonal plane superconduction is via the conventional means of Cooper pairs.

3.3. High Temperature Superconduction

High temperature superconductors, exhibiting superconductivity above 77K are unconventional in mode of operation. On the basis of the instant hypothesis, given that delocalisation is already present at higher temperatures due to a structure which promotes electron sharing and thus delocalisation; there is less need for the profound temperature nadirs of conventional superconductors to elicit quantum effects of the Cooper pair. We submit that lower temperatures in unconventional superconductors reduces electron and nuclear excursions thus prevent capture of an electron by nucleus if it veers within its electromagnetic orbit. However, where the delocalisation is so intrinsic to structure and electron sharing irrefragably committed; temperature reductions may

need only be modest if at all. This opens the tantalising possibility of room temperatures superconductivity, which has been suggested with highly aligned pyrolytic graphite.

4. Water Leads the Way

The empiric phenomenon we describe here of delocalised and shared charged particles effecting superconductivity is observed in proton transfer in water. It manifests in the enigmatic Grotthuss mechanism on en mass proton hopping when combined with Nuclear Quantum Effects (NQE). Of all fluids water has unique characteristics due the combination of hydrogen bonding and NQE. The diminutive size of the hydrogen atom nucleus means that quantum effects have a demonstrable and tangible impact on behaviour [17–19].

Water forms a network of connections via hydrogen bonding, the electron lone pairs are bound to the hydrogen of adjacent molecules. Due to the Nuclear Quantum Effects (NQE) of the proton, it is not apparent which proton belongs (covalently bonded) to which oxygen and which proton is merely hydrogen-bonded to which oxygen. Now when protons are added the elegance of the system is even more pronounced. Oxygen lone pairs bind to the protons. However, as a function of NQE of water, it is not clear which hydrogen constitutes the proton and which constitutes a hydrogen atom bound to oxygen in water. Mouhat et al showed that at around the temperatures found on planetary earth including room and body temperature the short Zundel is pre-eminent [20] (Figure 6). Here the proton is perfectly shared between two oxygen atoms of two water molecules. Proton transfer is adiabatic. Temperature is critical for this. It must be sufficiently high for adjacent water molecules to sufficiently proximate to overcome repulsive forces. However it must not be so elevated such that proton excursions are sufficiently large that the latter become sequestered and trapped in the electromagnetic field of one of the flanking oxygen species. Due to NQE this critical temperature window is relatively broad. Movement of this nexus of protons is adiabatic requiring no energy to overcome and flanking attraction of adjacent lone pairs. The proton is an energy trough. As the temperature rises oxygen species cans separate and proton motion can lead the later appropriated by adjacent molecule. An energy hurdle must then be overcome to transfer to the next molecule.

The remarkable element is that this adiabatic movement of protons occurs at room temperature. This may have profound implications for life and evolution itself. Mouhat et al reported peak proton migration between 250K and 300K, with body temperature at 310K being just beyond the apogee.

Experimental support of this was provided by Wang et al. They reported exceptionally high conductivity of planer water nanometres in depth in physiological conditions [21].

5. Confirmation of Quantum Chemiosmosis

A striking application of this phenomenon is in the subcellular structure the mitochondrion and indeed in chloroplasts. Mitochondria produce energy for cells. The fundamental substrate for that is the movement of hydrogen ions down a concentration gradient across specific ion enzyme-channels, ATP synthase, which transduces this energy. This process is problematic if not impossible under classical chemistry. The mitochondrion is exceptionally small. Hence although the pH is low, given the size of the relevant space at a pH of 6.8 there are only 7 protons under a classical paradigm [22]. This is compounded by the fact that the transit of three protons is required for the generation of 1 molecule of ATP [23].

Further the “energy turn-style”, namely the ATP synthase molecules, that the proton must traverse, occupies a minority of the membrane space and is located in crypts known as cristae. The probability of the 7 protons finding the ATP synthases by stochastic diffusion is low and the necessary time period too protracted for life. However under proton superconductivity paradigm it is inevitable. In this context the protons are shared due to hydrogen bonding and NQEs: it is not clear which proton is the hydrogen ion and which constitutes part of a water molecule. The proton does not travel from location in the mitochondria to the ATP synthase but it already exist juxtaposed to

the ATP synthase in the form of the hydrogen atom of the water molecule nearest to this enzyme. NQE also reduce an effective pH giving the “quantum pH” by autocatalysis [24].

Astronomically high rates of proton transfer have been observed across proton channel moiety of ATP synthase, in excess of 6200 protons per second. This far exceeds that which is possible by stochastic diffusion. Using the recorded pH gradients of 0.3-0.7 the mitochondrion has an efficiency of 124% [25]. This is impossible without the implication of quantum mechanics.

The exploitation of this guise of superconduction has been termed quantum chemiosmosis [26]. It evidenced by the fact that efficiency of the mitochondria has consistently been reported at greater than 100% and the generation of ATP when the proton motive force should be subliminal and thus the process enthalpically impossible [27].

6. Quantum Siphon

Mutual exclusivity is not a feature of quantum phenomena. Rather it is characterised the co-existence and duality of incompatible states. With this regard BCS theory and Adiabatic Delocalised Shared Electron Transfer (ADSET) may not be entirely immiscible concepts. A potential difference causes a shift in the electron cloud. This transiently leaves a “vacuum” which manifests as a positive charge or phonon into which the adjacent electron cloud migrates. The system can then continue ad infinitum akin to a “quantum siphon”. A siphon classically describes a system whereby two fluids are connected by a tube or some other conduit; often one is at varying degrees of higher vertical elevation or altitude than the other [28]. Once flow is initiated via transient reduction in pressure in the lower end of the conduit, it continues until the superior vessel is emptied. The system functions via an effect of gravity, the cohesive properties of the fluid especially if water and atmospheric pressure; either individually or in combination. Analogous methods are operative in the case of delocalised electrons. Significant energy introduction is required to isolate a single electron from the cloud. Consider in the case of benzene this would involve destroying the entire ring, which is hugely enthalpically unfavourable. Hence the potential difference pulls the entire cloud en masse due it is “quantum cohesive force”. This is equivalent in principle to the energy required to separate Cooper pairs.

7. Strange Metals Demystified

Strange metals exhibit many behaviours of unconventional superconductors [29]. In addition they classical display a linear increase in resistivity with increase in temperature with the lower temperature range. ADSET perfectly accounts for these para-phenomena. “Normal” metals show a quadratic relationship between temperature and resistivity above the critical temperature. This is due to electron interaction and in particular electron-electron scattering. However at higher temperature where this engagement is less pronounced Normal metals display a linear relationship. Now given that unconventional superconduction is predicated on the movement of delocalised electrons analogous to benzene. There exist no possibility of electron-electron scattering and thus only a linear relationship between resistivity and temperature are observed.

8. Dielectric Dilemma Explicated

Unconventional superconductors, expressly the organic and cuprate superconductors are characterised by high dielectric constant [30]. This is consistent with their mechanism of action. The dielectric is an index of the ability of a material to store charge and its polarisability. In an electric field polarisable species align themselves in a configuration such the negative polarity faces the positive terminal and the negative towards the anode. Materials are known to have extremely highly dielectric constants in excess of the materials most adepts at storing charges. This is due to the delocalised electrons which realign the probability cloud in the face of the electric charge. A similar paradigm explains the large dielectric constant observed with.

9. Thouless Pump in Chemiosmosis?

This phenomenon first evinced by David Thouless [31] in 1983 and considered further by Qian Niu [32] in 1984 describes specifically the adiabatic quantized transfer of charge essentially in the absence of potential gradient [33]. The classical example is the slow-moving alternating current. A current translocates adiabatically in the direction of the AC current. Under a classical paradigm the electrons remain ultimately in the same position. However, in the mobile AC current, in a quantum paradigm, electrons have access to lower energy levels as the waves elide as the AC travels. They exploit this to travel with no net potential gradient. Indeed, chemiosmosis in some guises acts in a manner similar to a Thouless pump. When the proton is viewed as a wave, the extrusion of protons to juxta—membrane space by slow-moving ponderous cytochrome species causes an elision of waves and enable protons to pursue lower energy levels their transfer thus have adiabatic component notwithstanding the any proton motive force. This is non-Abelian (non-commutative) Thouless pump as the electron transport has directionality for ATP generation [34]. A number of studies have strongly suggested the operation of a mechanism akin to the Thouless pump in mitochondria. Troth et al reported no robust ATP synthesis in a synthetic liposome with ATP synthase, notwithstanding an electrochemically propitious milieu with adequate proton motive force [35]. However, following the introduction of cytochrome species a proton current was generated with concomitant ATP synthesis, in spite of there being no alteration to the proton motive force with the subliminal membrane potential generating a cycle of delocalised protons in the juxta-membrane layer of the mitochondrion. It is submitted that the extrusion of protons, which act as waves via the cytochrome species mimics the Thouless pump by generating over-lapping waves allowing mitochondria to migrate exploiting lower energy levels. Wiedenmann made an identical observation in Troth et al in *E. coli* [36]. Guffani *et al* reported even in the presence of a proton-motive force insufficient to generate ATP synthesis, ATP generation persisted in alkalophile bacterium *Bacillus firmus* OF4 [37]. The Thouless mechanism can account for a current in this context.

Indeed evidence shows that the Zundel motif predominates and actually concentrates to the interfacial area [38,39]. Yang reported the proton intercedent between the two oxygen species vacillates between the two adiabatically with no energy expended and occupies every space in less than 100 femtoseconds The superimposition of a proton motive force will elicit and mobile AC current akin to the Thouless pump.

10. Thouless Pump – Unravels the Mystery of Twisted Graphene

One of the most numinous and newest features of superconductors is the enigmatic finding that twisting two lattices, classically of graphene, to a critical angle, which is modest and of in the region of 1.1o produces superconductivity [40]. This is accommodated by our hypothesis. Within the Thouless pump paradigm. Twisting creates π orbitals at differing orientations and variations, the passage of a voltage simulates overlapping probability and energy levels allowing electrons to access lower energy levels to migrate adiabatically. Indeed the twisting of layer of graphene against the other generates a Thouless pump current migration [41,42]. In the absence of the twist π electrons are superimposed. However with p orbital electrons, normal to the plane, from superior and inferior laminae are juxtaposed. There is a point where p orbitals from homo-planar carbons cannot be distinguished from those hetero-planar carbons [43]. This necessarily occurs at modest angles of gyration. At very large angles the p orbital from adjacent laminae are widely separately. At modest angles they move from superimposition and repulsion to juxtaposition and confluations. This is theoretically not possible with the cuprates given the structures between the conducting laminae.

11. Conclusions

ADSET convincingly accounts for a number of features of superconduction including the modus operandi of unconventional superconductors, Type II superconductors and high temperature superconductors. Delocalised, shared electrons “travel” between lamina but in reality “each electron”

already occupies the space it ventures into. Each lamina consists of polygonal units which can allow sufficiently large magnetic field to penetrate, creating vortices. These para-phenomena cannot be accommodated with the BCS quantum Weltanschauung. The structural features of unconventional superconductors “transfix” electrons in a quantum state of shared indivisible electrons, at comparatively high temperatures, raising the possibility of room temperature superconduction. The very existence of life itself may have depended upon an analogous phenomenon in water with Nuclear Quantum Effects, hydrogen bonding and the Grotthuss mechanism emulating a superconductive state of protons in water especially in a juxta-membrane milieu.

Figure 1: Energy barriers for electrons to migrate between two nuclei with perfect sharing (purple) and without sharing (blue).

Figure 2: Benzene ring from https://en.wikipedia.org/wiki/Benzene#/media/File:Benzene_Representations.svg

Figure 3: Cuprates from https://en.wikipedia.org/wiki/High-temperature_superconductivity#/media/File:Ybco.jpg

Figure 4: Conduction of Type II superconductor with varying temperature T and magnetic field H . T_c : transition temperature below above material is standard conductor. HC_1 : Magnetic strength above which the magnet penetrates the material and induces standard conduction. HC_2 : Magnetic strength above which Type II conductors exhibit partial penetration and vortices.

From <https://www.doitpoms.ac.uk/tlplib/superconductivity/type.php>

Figure 5: Type II superconductors operative between magnetic field strengths of HC_1 and HC_2 . From <https://www.doitpoms.ac.uk/tlplib/superconductivity/type.php>

Figure 6: Zundel Motif of perfect sharing. From <https://www.nature.com/articles/s41467-023-42366-4/figures/1>.

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