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Searching for high-temperature superconductivity: from Mendeleev to Seiberg–Witten via Madelung and beyond

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Recently, noticeable progress has been achieved in the area of high-temperature superconductors. Maximum temperatures T_c of 250 K (−23° C) for LaH_{10} and 288 K (+15° C) for CSH_8 have been reported at megabar pressures. The highest possible T_cs were achieved by employing hydrides of chemical elements. Empirically, many of these are made of Madelung-exceptional atoms. Here, the theoretical background is provided to explain this observation. The, thus far empirical, Madelung rule controls Mendeleev's law of periodicity. Although the majority of elements do obey this rule, there are some exceptions. Thus, it is of interest to derive it and its exceptions theoretically in view of experimental findings. As a by-product, such a study yields a plausible explanation of the role of Madelung-exceptional atoms in the design of high-T_c superconductors. Thus far the atoms obeying the Madelung rule and its exceptions have been studied with help of relativistic Hartree–Fock calculations. In this work we reobtain both the rule and the exceptions analytically. The newly developed methods are expected to be of value in quantum many-body theory and, in particular, in the theory of high-T_c superconductivity. Ultimately, the new methods involve some uses of the Seiberg–Witten theory known as the extended Ginzburg–Landau theory of superconductivity. Using results of Sieberg–Witten theory, the difference between Madelung-regular and Madelung-exceptional atoms is explained in terms of the topological transition. The extension of this single-atom result to solids of the respective elements is also discussed.

Subject Index A13, A63, E01, I64, I67

1. Introduction

1.1 *Not too widely known facts about atomic superconductivity*

The most essential feature of superconductivity is the Meissner effect—the expulsion of a superconductor from an applied static magnetic field. Such a feature makes all superconductors diamagnetic. With respect to the external magnetic field all atoms exhibit magnetic properties as well. It is not immediately clear, though, whether the magnetic properties of individual atoms survive if they form the bulk solid phase. Hydrogen, the simplest chemical element, already exhibits a variety of puzzling properties. Although it is studied in every course on quantum mechanics, standard treatments imply that atomic hydrogen should be both paramagnetic (strongly) and diamagnetic (weakly). In reality, it is diamagnetic only. That is, atomic hydrogen is already a superconductor! If this is so, will this property survive for solid hydrogen? Surprisingly, there is no mathematically rigorous answer to this question.

The standard methods of quantum mechanics indicate that paramagnetism should exist for hydrogen. And, indeed, all other hydrogen-like atoms, e.g. Li, Na, K, Rb, Cs, are indeed paramagnetic, as experiment and elementary calculation demonstrate. Furthermore, the surprising atomic diamagnetism of hydrogen is followed by the much anticipated diamagnetism of He and Be. These observations are misleading, though. Indeed, all noble gases are diamagnetic, as is Be, but they are not practical superconductors in bulk, and Be under normal ambient pressures is a very bad superconductor. Thus, bulk superconductivity implies diamagnetism, but the opposite is not true. The diamagnetism of atomic hydrogen is the subject of hundreds of publications. It can be explained group-theoretically [1], using the theory of quantum chaos [2], or through perturbation theory of superintegrable systems.[1]

The diamagnetism of atomic H and paramagnetism of Li, Na, K, Rb, and Cs seemingly affects their phase diagrams. Li, Na, K, Rb, and Cs readily become metals under normal pressures, while for H this is not possible. In 1935, Eugene P. Wigner and Hillard B. Huntington [4] predicted that only at pressures above 25 GPa would hydrogen become an alkali metal-like solid. Some (but not all!) alkali metals under similar pressures will become superconducting [5]. Ashcroft (in 1968) and, independently, Ginzburg (in 1969) predicted that metallized hydrogen is an ideal candidate to exhibit high-T_c superconductivity [5]. Although superconducting hydrogen has not yet been found reliably, many theoretical predictions do exist indicating that superconducting hydrogen might exist at pressures above 450–500 GPa at room temperature and above. Its superconductivity is believed to be described by the well-studied Bardeen–Cooper–Schrieffer (BCS) theory and/or its Migdal–Eliashberg modification. The question that immediately emerges is whether there is a way to reduce the pressures for hydrogen while retaining superconductivity?

The important step in this direction was made by Gilman in 1971 [6]. He suggested using hydrides, XH_n, where X is an atom other than hydrogen and n is the number of hydrogen atoms attached to it, perhaps under high pressure.[2] Gilman's idea to use hydrides instead of hydrogen was named *chemical precompression*. The idea seemed very attractive because of the following logic behind it: (i) Take an element (metal or not), (ii) apply pressure to it until it becomes a solid, and (iii) at stages (i) and/or (ii) try to saturate this solid with atomic hydrogen. Such saturation will eventually create a hydrogen sublattice[3] inside the host lattice. The sublattice will force the hydrogen to act like a solid and, hopefully, this solid will be superconducting under mild readjustment of external parameters.

From the description of precompression, several questions emerge: How to make an alloy with a prescribed number n of hydrogen atoms? Is there any relationship between n, T_c, and the pressure? How stable are hydrogen sublattices? Since these topics were discussed in Ref. [5] this spares us from an extended discussion here. At the same time, since answering these questions brings us directly to the subject matter of this paper, we present some additional comments in the next subsection.

[1] For example, read the definition of superintegrability in [3]. The study of the sophisticated perturbational theory of superintegrable systems is also mentioned in [3].

[2] In practice, n may not be an integer.

[3] There could be more than one sublattice.

1.2 *Reversible hydrides: The peculiar interplay between atomic and bulk superconductivities studied with Bogoliubov's method of quasiaverages*

In the previous subsection we learned that hydrogen, the lightest atomic superconductors, is expected to yield under very high pressures the highest possible T_c. Even if this result is achieved in the laboratory, extremely high pressures make such a project of academic interest only. We do not discuss here situations inside stellar or planetary cores leading to the emergence of the permanent magnetic field around these objects. Thus, focusing attention on hydrides makes more sense. But the problem of how to make an alloy with a prescribed number of hydrogen atoms still remains, and hence some requirements should be applied to make the correct selection of the atom X.

According to [5, p. 45], "in order to obtain the effective metallization of the hydrogen sublattice, it would be more convenient to start from the existing hydrogen-rich molecule since in this case the hydrogen does not have to be incorporated into a host metal lattice." No examples of such hydrated molecules are given in Ref. [5].[4] At the same time, Ref. [5, p. 5] comments on the relationship between n, T_c, and the pressure as follows: "The possibility of predicting T_c from first principles played a crucial role in the second hydride revolution (dawn of the 2000s) as well as the development of computational tools to predict the crystal structures and phase diagrams of materials under given thermodynamic conditions." Nevertheless, Ref. [5, p. 47] has the following clarification: "rare-earth and actinides are theoretically challenging to describe, and one can quickly obtain wrong results..." But it is exactly these elements that are the Madelung-exceptional! They also yield hydrides with the highest T_cs. This quotation from Ref. [5] provides us with the first compelling reason to study further the Madelung-exceptional elements. Furthermore, the intuitive belief that the larger n is, the higher T_c should be does not always work for the following reason. Reference [5, p. 20] states: "systems containing light mass atoms, like hydrides under pressure, exhibit intrinsically large vibrational displacements and hence showcase a variety of effects due to strong anharmonicity..." Thus, if high T_cs cannot be achieved just by increasing n, the focus of attention shifts to the Madelung-exceptional elements for the following reason. This reason is historical; it is *not at all* motivated by the Madelung-exceptionality of elements.

In 1866 Thomas Graham discovered that at 1 atm metallic palladium can absorb hydrogen in large amounts: 0.58 H atoms per one Pd atom. Since that time, for more than 150 years the Pd–H_2 system has remained the benchmark model for studying metal hydrides, beginning with PdH_x [7]. For this historical reason, the study of superconducting hydrides began with hydrides of Pd and Th. Incidentally, although both are Madelung-exceptional, nowhere in the literature is this fact mentioned or emphasized. The motivation came from another observation. Under normal atmospheric pressure Pd is not a superconductor and Th is an exceptionally bad superconductor (it has $T_c = 1.374\,\mathrm{K}$ [8]. At the same time, the hydride PdH_x ($x \simeq 0.7$) is a superconductor, with $T_c \simeq 9\,\mathrm{K}$, and for $ThH_{3.84}$ T_c was found to be 8.35 K [9]. These results demonstrate that the use of hydrides is a step in the right direction. The problem, nevertheless, remains. Yes, PdH_x and $ThH_{3.84}$ had noticeably improved their T_cs. upon making hydrides, and for PdH_x T_c increases linearly with a linear increase in the fraction of H in PdH_x [5, p. 49]. But, is it possible to regulate the the amount of H in hydrides of other atoms to the extent it was done in Pd and Th?

[4] However, based on the results of this paper hydrated molecules made of Madelung-exceptional and hydrogen atoms are theoretically permissible.

Yes, computational advancements formally allowed the prediction of T_c for the assigned pressure, but to what extent can these hydrides be recreated in real life? And, as mentioned above, for Madelung-exceptional atoms the computations are not reliable but the T_cs obtained are among the highest. Because of this, we focus our attention on Madelung-exceptional atoms. In doing so, we shall cite extensively the contents of Refs. [10,11].

According to Ref. [10], molecular dissociation of H_2 is the first step toward the formation of hydrides by absorption. Other than Pd, most metals require energy input in order to overcome the activation barrier. This is achieved by the application of high hydrogen pressures and elevated temperatures. On Pd surfaces, the dissociative absorption of H_2 molecules occurs with *little or no activation energy barrier*! This fact causes the absorption to be reversible, and therefore, following Ref. [11], all hydrides for which the absorption is reversible are called *reversible hydrides*. Empirically, it is known [11, p. 31] that all the reversible hydrides working at around ambient temperature and atmospheric pressure consist of transitional and rare earth metals; that is, almost all of them are Madelung-exceptional! In particular, very good reversible hydrides are made of Pt and Ru [11]. What is the physics behind this phenomenon? The hint is given by the name: *reversible hydrides*.

To move forward, we need to have some model of the metal. This will enable us to describe the absorption–desorption process within the limits of this model. The simplest model of a metal is some weakly or strongly interacting electron gas on some jellium-like neutralizing background. It happens that the description of absorption–desorption processes based on such a model [12] make good sense. Irrespective of the ramifications of a given model, all models are subject to some constraints of a general nature. These are associated with symmetry. Conservation of energy, momentum, spin, etc. all are consequences of symmetry. More delicate are the conservation laws associated with, for example, the conservation of particles. These are connected with (global) gauge invariance symmetry. Also, it matters whether the particles are bosons or fermions. Photons, phonons, and plasmons are bosons, and they are massless. In superconductivity two fermions forming a Cooper pair become one boson. But this BCS boson is massive. Bogoliubov developed a very general concept of *quasiaverages* [13,14] in connection with his seminal works on superconductivity. It is essential to emphasize that this concept is far more general than just superconductivity problematics [14]. The concept of quasiaverages is useful whenever there is some change in symmetry. In the present case, we are dealing with a fermion system whose number of particles is not conserved.[5] This is indicative of the spontaneous breakage of the global U(1) symmetry associated with electromagnetism. Within the framework of superconductivity, details are provided in Sect. 6 and Appendix E.3.

The case of reversible hydrides falls into this category. Indeed, the absorption process begins with H_2 breaking into two H atoms, each having a proton and an electron. Both are fermions. When the pair of H atoms enters the bulk solid, it donates two electrons (fermions) to the interacting electron gas and two protons (fermions) to the jelly. Since the process is reversible, the two H atoms can emerge back at the surface. Since the bulk system is not particle conserving, such a reversible process requires no energy for it to happen. This picture is missing one very important ingredient: the absorption–desorption process just described is *not* valid for *all* solids (metallic or not)! It is only valid for solids made of hydrides of Madelung-exceptional atoms since these atoms (and only these!) are superconducting, as explained in Appendices E.4

[5] For example, a hydride molecule in the simplest case.

and E.5. In the previous subsection we argued that the H atom is also superconducting since it is diamagnetic. Since such Madelung-exceptional solids are reversible hydrides, this makes these solids nontraditional superconductors in the way just described. This makes sense because Pd is not a superconductor without H atoms. The presence of H, in whatever amounts, makes it superconducting in the conventional sense. The same is true for other Madelung-exceptional elements. The results just presented allow us to formulate the content of the rest of this work.

1.3 *Organization of the rest of the paper*

In Sect. 2 we present basic facts about atomic physics that allow us to introduce definitions of Madelung-regular and Madelung-exceptional atoms. In Sect. 3 we explain what makes Madelung-exceptional atoms exceptional. We argue that (a) Madelung-exceptionality is a relativistic phenomenon, and (b) the application of relativistic methods known in the physics literature makes all atoms Madelung-exceptional. This creates the first fundamental problem: how to disentangle the Madelung-exceptional atoms from the Madelung-regular? In Sect. 3 we explicitly explain what features make atoms Madelung-regular. In reading Sects. 2 and 3 the reader is encouraged to read Appendices A, B, and C; they are not optional! Section 4 is meant to prepare the reader for new information. For this purpose we have converted the results of Sect. 3 into an equivalent geometrical/topological form, allowing us to account for the effects of covariance, gauge invariance (local and global), etc. This conversion was influenced by the work of Schrödinger on the Dirac electron in a gravitational field. In doing so we have used the original work by Schrödinger [15], written in German, as well as its English translation [16]. The results of Sect. 4 allow us to bring into play the results of Seiberg–Witten (S–W) theory in Sect. 5. Although this theory, according to its author [17], is just a sophisticated extension of the Ginzburg–Landau theory of superconductivity, to our knowledge there have been no precedents, until this paper, explicitly demonstrating (using physical terminology) the connection of the S–W formalism with that for superconductivity. This is done here with the purpose of demonstrating that mathematically the transition from Madelung-regular to Madelung-exceptional atomic behavior is of a topological nature. The case of Madelung-regular atoms requires for its description the concept of a *spin* manifold, while Madelung-exceptional atoms can "live" only on *spin*^{c} manifolds. Since the *spin*^{c} and *spin* manifolds are topologically different, the transition from Madelung-regular to Madelung-exceptional atoms is topological in nature. The definition of *spin*^{c} manifolds in the mathematical literature [18] is devoid of any traces of physics. Being motivated by the physics of reversible hydrides, discussed in Sect. 1.2, we found a physical interpretation of *spin*^{c} manifolds in terms of known concepts of BCS superconductivity, e.g. using the Bogoliubov–De Gennes equations. Details are provided in Appendices D and E.

Finally, in Appendix F we further simplify the concept of *spin*^{c} manifolds and test this simplified definition using known examples of electron filling patterns for Madelung-exceptional and regular atoms. The S–W formalism also allows us to demonstrate, in Appendix C, that the number of Madelung-exceptional elements is always finite and always holds only for heavier atoms, where the relativistic effects are nonnegligible.

In Sect. 6 we discuss two problems: (a) the problem of extending the single-atom results just obtained to solids of macroscopic sizes, and (b) provided that problem (a) is solved, will these solids remain superconductive? Section 7 is devoted to a summary and discussion.

2. Some facts about the periodic system of elements

2.1 *Madelung-regular vs. Madelung-exceptional atoms*

Although the quantum-mechanical description of multielectron atoms and molecules is considered to be a well-developed domain of research, a recently published book [19] indicates that there are still many topics to be addressed. The quantum-mechanical description of a multielectron atom (with atomic number Z and infinitely heavy nucleus) begins with writing down the stationary Schrödinger equation,

$$\hat{\mathrm{H}}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z), \tag{1}$$

with the Hamiltonian

$$\hat{\mathrm{H}} = -\sum_{i=1}^{Z} \frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i=1}^{Z} \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{Z} \frac{e^2}{r_{ij}}. \tag{2}$$

Bohr's *Aufbauprinzip* postulates that the atom with atomic number Z is made of Z electrons added in succession to the bare atomic nucleus. At the initial stages of this process the electrons are assumed to occupy the one-electron levels of the lowest energy. Mathematically, this process is described in terms of the one-electron eigenvalue problem,

$$\hat{\mathrm{H}}_i\psi_{\square_i}(\mathbf{r}_i) = \left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{e}_\smile}(\mathbf{r}_i)\right]\psi_{\square_i}(\mathbf{r}_i) = \varepsilon_{nl}(i)\psi_{\square_i}(\mathbf{r}_i), \qquad i = 1 \div Z, \tag{3}$$

where $V_{\mathrm{e}_\smile}(\mathbf{r}_i)$ is made of the combined nuclear potential $-\frac{Ze^2}{r_i}$ and the centrally symmetric Hartree–Fock-type potential $\mathcal{F}(\mathbf{r}_i)$ for the ith electron coming from the presence of the rest of the atomic electrons. The fact that $\mathcal{F}(\mathbf{r}_i)$ is indeed centrally symmetric was demonstrated in Ref. [20]. It is fundamentally important for our calculations. The symbol $\square_i$ indicates the ith entry in the set made out of hydrogen-like quantum numbers for individual electrons. Based on this, the concept of an *orbital* is associated with the major quantum number n having its origin in studies of the hydrogen atom. In the quantum many-body system described by Eq. (3), however, it makes more sense to associate the concept of an orbital with the description of the somehow labeled (say, by interaction with a photon, when studied spectroscopically) the ith electron moving in the centrally symmetric potential $V_{\mathrm{e}_\smile}(\mathbf{r}_i)$. The quantum motion in such a potential should cause the hydrogen quantum numbers n, l, m, and m_s to change into *hydrogen-like*[6]since the hydrogen atom eigenvalue problem is now replaced by the eigenvalue problem for the labeled ith electron in the centrally symmetric potential $V_{\mathrm{e}_\smile}(\mathbf{r}_i)$, which is different from the Coulombic.

The actual implementation of this observation is presented in this work from a new standpoint. It is known that the number of electrons allowed to sit on such a redefined orbital is determined by the *Pauli exclusion principle*. With increasing Z the electrons are expected to occupy successive orbitals according to Bohr's *Aufbau* scheme until the final ground state electron configuration is reached. This is achieved by using the assumption made by Bohr that an atom with Z electrons is made from a atom with $Z-1$ electrons by (a) changing the nuclear charge by $+1$ and simultaneously adding one additional electron. In such an imaginary process it is assumed that the quantum numbers of electrons in the $Z-1$ atom remain unchanged [21].

The problem with the *Aufbauprinzip* just described lies in the assumption that the guiding principle in designing the final ground state electron configuration has two components: (a) knowledge of the hydrogen-like wave functions supplying (labeled by) the quantum

[6]See, for example, Sect. 3.3.

boxes/numbers $\square_i$, and (b) the Pauli principle mathematically restated in the form of fully antisymmetric wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)$. Although mathematically it is just an exterior differential form, the existing treatments do not use the Hodge–De Rham theory of differential forms to describe the Pauli principle. In this work this is corrected.

Should requirements (a) and (b) be sufficient, then the familiar hydrogen-like quantum numbers n, l, m, and m_s for hydrogen would make the filling of electronic levels proceed according to the Fock n-rule:

The Fock n-rule: With increasing Z, the nl orbitals are filled in order of increasing n.

This rule already leads to problems for lithium [19, p. 330]. As a result, the n-rule was replaced by the (n, l) rule:

The hydrogenic (n, l) rule: With increasing Z, the orbitals are filled in order of increasing n, while for a fixed n the orbitals are filled in order of increasing l.

After $Z = 18$ the (n, l) rule breaks down as well. Therefore, it was subsequently replaced by the $(n + l, n)$ rule of Madelung:

The Madelung (n + l, n) rule: With increasing Z, the orbitals are filled in order of increasing $n + l = N$. For fixed N, the orbitals are filled in order of increasing n.

This rule was included by Madelung in Ref. [21] in the form of Appendix 11 describing the filling of the periodic table. In the same Appendix 11 Madelung confesses that: (a) the filling rule is strictly empirical, and (b) as such, it does possess some exceptions. The Madelung rule and its exceptions require theoretical explanation.

By organizing the elements in periods of constant $n + l$ and in groups of constant l, m_l, and m_s, period doubling emerges naturally and leads to the sequence of periods 2–2–8–8–18–18–32–32. Using the apparatus of dynamical group theory in Ref. [19], the period doubling was recreated. The application of group-theoretic methods to periodic systems has occurred repeatedly in the past. To our knowledge, the most notable results are presented in [22, Chapter 6]. Much later, those results were independently reobtained in Ref. [19]. Should the Madelung rule be without exceptions, the results just mentioned would be sufficient. However, the existing exceptions for some transition metals, lanthanides, and actinides indicate that the use of dynamical group theory methods alone is not sufficient. As result, in this work we describe alternative methods enabling us to explain the Madelung rule and its exceptions.

The problem of finding a theoretical explanation of the Madelung rule attracted the attention of Demkov and Ostrovsky (D–O) [23]. They used methods that were not group theoretic, enabling them to guess $V_{\text{e}_\sqcup}(\mathbf{r}_i)$ correctly. This was achieved by taking into account the implications of the Bertrand theorem of classical mechanics [24]. It imposes apparently insurmountable restrictions on the selection of $V_{\text{e}_\sqcup}(\mathbf{r}_i)$: for spherically symmetric potentials only the Coulombic $-\frac{Ze^2}{r_i}$ and the harmonic oscillator kr^2 potentials allow dynamically closed orbits. The theoretical treatment of multielectron atoms before D–O was confined either to the study of spectra of classically and quantum mechanically chaotic systems or to uses of variational (relativistic or otherwise) Hartree–Fock spectral calculations. Beginning with the motion of electrons in the helium atom, the classical (and, hence, the semiclassical!) dynamics of electrons in multielectron atoms is believed to be chaotic. The seminal Ref. [25] is an excellent introduction to this topic. Bethe and Jackiw [20] had already noticed that the Hartree–Fock $V_{\text{e}_\sqcup}(\mathbf{r}_i)$ is centrally symmetric. This brings into question the issue of the description of a multielectron atom at the

semiclassical level. D–O found a seemingly innovative approach to the spectral problem. They applied the optical–mechanical analogy in which the Maxwell fish-eye potential was used instead of the Coulombic potential for the hydrogen atom. D–O believed that such a replacement might help them to cope with the multielectron effects while maintaining agreement with the Bertrand theorem. To do so, they (a) replaced the Coulomb potential by the fish-eye potential, and (b) used conformal transformations applied to the fish-eye potential aimed at conformally deforming this potential in such a way that it correctly represented the multielectron effects. At the level of classical mechanics D–O demonstrated the equivalence (for the hydrogen atom) between the Hamilton–Jacobi equations employing the Maxwell fish-eye and the Coulombic potentials. In Appendix B we reproduce the necessary details and comment on some flaws in the D–O reasoning. At the quantum level D–O believed that "The Maxwell's fish-eye problem is closely related to the Coulomb problem." Being aware of Ref. [26], D–O nevertheless underestimated the nature of the connection between the Coulombic and optical (fish-eye) problems. The assumption of only a "close relationship" caused D–O to replace Eq. (3) with

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{e_\sqcup}(\mathbf{r}_i)\right]\psi(\mathbf{r}_i) = 0. \tag{4}$$

Equation (4) looks different from Eq. (3). Equation (3) is an eigenvalue spectral problem, while Eq. (4) is the Sturmian problem. That is to say, for the Sturmian-type problem to be well defined, the parameters entering into $V_{e_\sqcup}(\mathbf{r}_i)$ must be quantized. Such quantization of parameters makes Sturmian and eigenvalue problems equivalent. To prove this equivalence is nontrivial but possible; it was overlooked by D–O. Reference [3] demonstrates that even though Eqs. (3) and (4) produce exactly the same spectrum, only Eq. (4) can be subjected to conformal transformations while Eq. (3) cannot. That such transformations lead to the correct reproduction of multielectron effects and are compatible with the extended Bertrand theorem is also demonstrated in Ref. [3]. Compatibility with the Bertrand theorem had become possible only thanks to the seminal work of Ref. [27], in which the results of the classical Bertrand theorem [24] valid in flat Euclidean three-dimensional space were extended to static spherically symmetric spacetimes of general relativity. By design, the motion in such curved spacetimes takes place on closed orbits. Thus, our task was to demonstrate that the classical/semiclassical limit of Eq. (4) with the appropriately deformed D–O potential leads to the motion in generalized Bertrand spacetimes found in Ref. [27]. In Ref. [3] such a demonstration was performed. Thus, for the first time the place of gravity effects in a testable realistic quantum-mechanical problem was found.[7] In addition, in Ref. [3] the connection between the deformed D–O potential and the Hartree–Fock $V_{e_\sqcup}(\mathbf{r}_i)$ potential was found. These achievements enable us to make the further progress described in this work.

3. Beyond the canonical Madelung rule

3.1 *The origin of the Madelung rule anomalies*

In the previous section we defined the Madelung rule. The opposite of this definition can be taken as the definition of Madelung-exceptions. Reference [19] leaves us with the impression that the correct mathematical understanding of the empirical Madelung rule can be obtained only using results from dynamical group theory, while the D–O results suggest an alternative

[7] More accurately, following J. A. Wheeler, we have to use the term "geometrodynamics" instead of gravity. Recall, that Wheeler's geometrodynamics is just an elaboration on the unified theory of gravity and electromagnetism proposed by G. I. Rainich in 1925.

approach which was significantly improved in Ref. [3]. If this is so, is there in this formalism room for the description of Madelung-exceptional elements?

From Sect. 1, it follows that the Madelung exceptions are observed among some transition metals, lanthanides, and actinides. The electronic structure of these elements has been studied thus far with the help of the relativistic Hartree–Fock methods [28]. A major new problem emerges: Will the results of solving Eq. (4) developed in detail in Ref. [3] survive the relativistic extension? Only such an extension may yield results compatible with that for the Madelung-exceptional atoms. The most difficult issue in doing so is the following: Since the nonrelativistic results already obtained are capable of deriving the regular Madelung rule quantum mechanically, the relativization of these results will make all chemical elements anomalous since the standard [28] formalism works indiscriminately for all atoms.

The S–W theory helps to solve this puzzle. This can be achieved in several steps.

3.2 *Preparing the nonrelativistic results for relativistic extension*

This extension can be achieved by using some facts about the quantization of the hydrogen atom model Hamiltonian that are not well known. These results will serve as a reference point. In particular, in a specially chosen system of units the dimensionless Hamiltonian $\hat{\mathrm{H}}$ for the hydrogen atom is given in the operator form as

$$\hat{\mathrm{H}} = \mathbf{p}^2 - \frac{2}{r}. \tag{5}$$

The Laplace–Runge–Lenz vector $\mathbf{A}_0$ is given by

$$\mathbf{A}_0 = \frac{\mathbf{x}}{r} + \frac{1}{2}(\mathbf{L}\times\mathbf{p} - \mathbf{p}\times\mathbf{L}), \tag{6}$$

with the angular momentum operator $\mathbf{L}$ defined as usual by $\mathbf{L} = \mathbf{x}\times\mathbf{p}$. It is convenient to normalize $\mathbf{A}_0$ as follows:

$$\mathbf{A} = \begin{cases} \mathbf{A}_0(-H)^{\frac{1}{2}} & \text{for } E < 0, \\ \mathbf{A}_0 & \text{for } E = 0, \\ \mathbf{A}_0 = (H)^{\frac{1}{2}} & \text{for } E > 0. \end{cases} \tag{7}$$

Here it is assumed that $\hat{\mathrm{H}}\Psi_E = \mathrm{E}\Psi_E$ and $\mathrm{E} = H$. By introducing two auxiliary angular momenta $\mathbf{J}(\alpha), \alpha = 1, 2$, such that $\mathbf{J}(1) = \frac{1}{2}(\mathbf{L} + \mathbf{A})$ and $\mathbf{J}(2) = \frac{1}{2}(\mathbf{L} - \mathbf{A})$, and using known commutation relations for $\mathbf{L}$ etc. we arrive at

$$\mathbf{J}(\alpha)\times\mathbf{J}(\alpha) = i\mathbf{J}(\alpha), \qquad \alpha = 1, 2,$$
$$[\mathbf{J}(1), \mathbf{J}(2)] = 0. \tag{8}$$

Taking into account that $\mathbf{L}\cdot\mathbf{A} = 0$ we also obtain two Casimir operators: $\mathbf{L}\cdot\mathbf{A} = 0 = \mathbf{A}\cdot\mathbf{L}$ and $\mathbf{L}^2 + \mathbf{A}^2$. The Lie algebras $\mathbf{J}(\alpha)\times\mathbf{J}(\alpha) = i\mathbf{J}(\alpha), \alpha = 1, 2$, are the algebras of rigid rotators for which the eigenvalues j_α $(j_\alpha + 1)$ are known from standard texts on quantum mechanics. The peculiarity of the present case lies in the fact that $\mathbf{J}(1)^2 = \mathbf{J}(2)^2$. This constraint leads us to the requirement $j_\alpha = j_\beta = j$. The topological meaning of this requirement is explained in [3]. In short, the eigenvalue equation for the standard quantum-mechanical rigid rotator is that for the Laplacian living on a two-sphere S^2. Since in the present case we have two rigid rotators, each of them should have its own sphere S^2. However, the constraint $j_\alpha = j_\beta = j$ causes these two spheres to be identified with each other pointwise. Topologically, such a pointwise identification leads to the three-sphere S^3. Group theoretically, the same result can be restated as $so(4) \simeq so(3)\oplus so(3)$.

With this background we are ready to relativize these results.

3.3 *Sketch of the derivation of the Madelung-regular rule*

To make sure that our relativization procedure is compatible with previously obtained results [3], we begin by restoring these results in a new fashion using the results of the previous subsection. For this purpose, the observation that the three-dimensional rigid rotator has the eigenvalues and eigenfunctions of the Laplacian "living" on an S^2,

$$\mathbf{L}^2 Y_{lm}(\theta,\phi) = l(l+1)Y_{lm}(\theta,\phi), \tag{9}$$

is helpful. Notice, however, that $\mathbf{L}^2 = \mathrm{L}_x^2 + \mathrm{L}_y^2 + \mathrm{L}_z^2$ and $\mathrm{L}_x = iD_{23}$, $\mathrm{L}_y = iD_{31}$, $\mathrm{L}_z = iD_{12}$, where

$$D_{\alpha\beta} = -x_\alpha \frac{\partial}{\partial x_\beta} + x_\beta \frac{\partial}{\partial x_\alpha}, \qquad \alpha < \beta = 1, 2, \ldots, d, \tag{10}$$

and d is the dimensionality of space. Now let $\mathrm{A}_x = iD_{14}$, $\mathrm{A}_y = iD_{24}$, $\mathrm{A}_z = iD_{34}$. If $\mathbf{L}^2$ represents the Laplacian on S^2, the combination $\mathbf{L}^2 + \mathbf{A}^2 \equiv \mathcal{L}^2$ represents the Laplacian on S^3 embedded in four-dimensional Euclidean space [22]. That is, instead of the more familiar study of a three-dimensional rigid rotator "living" on the two-sphere S^2, the eigenvalue problem for the hydrogen atom in fact involves studying the spectrum of the rigid rotator on S^3. This fact was realized initially by Fock [29]. The three Euler angles α, θ, and ϕ on S^3 replace the more familiar θ, ϕ angles used on the two-sphere.

The eigenvalue, Eq. (9), is now replaced by

$$\mathcal{L}^2 Y_{nlm}(\alpha,\theta,\phi) = I_{nl} Y_{nlm}(\alpha,\theta,\phi). \tag{11a}$$

This result coincides with that obtained in Appendix C, Eq. (C1). Here we have manifestly spherically symmetric wave functions with indices n, l, m. This result is immediately applicable to the hydrogen atom [22]. It corresponds to the choice $\gamma = 1$ in Eq. (C5). The choice $\gamma = 1/2$ in the potential, Eq. (B4), results in a shift in the indices in Eq. (11a) leading to

$$\mathcal{L}^2 Y_{n+l,lm}(\alpha,\theta,\phi) = I_{n+l,l} Y_{n+l,lm}(\alpha,\theta,\phi) \tag{11b}$$

in accord with the qualitative arguments made in Sect. 2. In spite of the apparent simplicity of the transition from Eq. (11a) to Eq. (11b), and taking account of the results of Appendices B and C, lengthy calculations [3] are still required. For the hydrogen atom the spectrum associated with Eq. (11a) is obtained in Appendix C, Eq. (C3), hile for the multielectron atom obeying the regular Madelung rule, the spectrum associated with Eq. (11b) is given below, in Eq. (27). Now we are in a position to develop the theory explaining the Madelung-exceptional atoms.

3.4 *Uncovering the source of the Madelung rule exceptions via relativization of previous results*

This task can be completed in several steps. First, we notice that in the standard three-dimensional calculations the hydrogen spectrum is determined by the eigenvalues of the *radial equation*

$$\left[-\frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right) + V(r)\right] R_{El}(r) = E R_{El}(r). \tag{12}$$

Here, the total wave function $\Psi_E = F_{El}(r)\mathcal{Y}_{lm}(\theta,\phi)$, $\mathcal{Y}_{lm}(\theta,\phi) = r^l Y_{lm}(\theta,\phi)$, $R_{El}(r) = r^l F_{El}(r)$, and $V(r) = -\frac{Ze^2}{r}$, $m = 1$, $\hbar = 1$. The combination $F_{El}(r)\mathcal{Y}_{lm}(\theta,\phi)$ can be rewritten in terms of $Y_{nlm}(\alpha,\theta,\phi)$ as demonstrated in Ref. [3] in accord with Ref. [22]. Therefore, it is sufficient to look at three-dimensional results. They can always be mapped into S^3 via inverse stereographic

projection. Next, this observation allows us, following Refs. [30,31], to use the Pauli matrices σ_i in order to rewrite $\mathbf{L}^2 = (\sigma \cdot \mathbf{L})(\sigma \cdot \mathbf{L} + 1)$. This identity permits us then to write the total momentum $\mathbf{J}$ as $\mathbf{J} = \mathbf{L} + \frac{1}{2}\sigma$. After that, it is convenient to introduce the operator $\mathcal{K} = \sigma \cdot \mathbf{L} + 1$ already used by Dirac [32] in his treatment of the hydrogen atom with the help of the Dirac equation. Using this operator it is possible to obtain the identity $\mathcal{K}^2 = \mathbf{J}^2 + \frac{1}{4}$, $\hbar = 1$. The eigenvalues of $\mathcal{K}$, denoted as κ, are known to be $\kappa = \pm 1, \pm 2, \ldots$ (0 is excluded). Use of these results implies:

$$l = l(\kappa) = \begin{cases} \kappa & \text{if } \kappa \text{ is positive,} \\ |\kappa| - 1 & \text{if } \kappa \text{ is negative,} \end{cases}$$

$$j = j(\kappa) = |\kappa| - \frac{1}{2}. \tag{13}$$

The above results were presented with a purpose not discussed at all in the standard texts on quantum mechanics. Specifically, at the classical level the Kepler trajectories can be determined with help of the vector $\mathbf{A}$ only [33]. This fact suggests that the quantum analog of $\mathbf{A}$ should produce an eigenvalue spectrum identical to that obtained using Eq. (12). This is indeed the case. To demonstrate this, we introduce the operator $\mathcal{N}$ such that $(\mathcal{N})^2 = (\sigma \cdot \mathbf{A})^2 + (\mathcal{K})^2$. Since it can be shown that $\sigma \cdot \mathbf{A}$ and $\mathcal{K}$ anticommute, it also becomes possible to write

$$\mathcal{N} = \sigma \cdot \mathbf{A} + \mathcal{K}. \tag{14}$$

Denote the eigenvalues of $\mathcal{N}$ as $\pm N$. Then, it is possible to demonstrate that

$$\sigma \cdot \mathbf{A}|N, \varkappa, m\rangle = (N^2 - \varkappa^2)^{1/2}|N, -\varkappa, m\rangle. \tag{15}$$

It is also possible to demonstrate that $N \rightleftarrows E$ with E as defined in Eq. (12). With the help of this result it is then possible to write the exact equivalent of the radial equation, Eq. (12). It is given by

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\mathcal{K}(\mathcal{K}+1)}{r^2} + \frac{2Ze^2}{r} - k^2\right]F_{N,l(\kappa)}(r) = 0. \tag{16}$$

Here, $k^2 = 2|E|$, $m = 1$, $\hbar = 1$. Reference [31] explains how the wave function $|N, -\varkappa, m\rangle$ is related to $F_{N,\,l(\kappa)}(r)$. Also, $\mathcal{K}(\mathcal{K}+1) = l(\kappa)(l(\kappa)+1)$.

The results just presented not only demonstrate that the quantum version of the Laplace–Runge–Lenz operator leads to an eigenvalue problem identical to the standard eigenvalue problem, Eq. (13), for the hydrogen atom presented in every textbook on quantum mechanics, but, in addition, they also permit us to perform their relativization in the most natural manner, thus allowing a seamless match of relativistic results with those known from nonrelativistic quantum mechanics.

The control parameter of this relativistic generalization is the fine structure constant $\alpha = \frac{e^2}{c\hbar}$. In the limit $\alpha = 0$, Eq. (16) is recovered as required. Since it is structurally identical to Eq. (12), the nonrelativistic spectrum is preserved. For $\alpha > 0$, Eq. (17) is replaced by a very similar equation,

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\Gamma(\Gamma+1)}{r^2} + \frac{2\alpha ZE}{c\hbar r} - k^2\right]\Phi_{N,l(\gamma\kappa)}(r) = 0. \tag{17}$$

Here, to avoid confusion when comparing with the original sources, we have restored $\hbar$, c, and m. In particular, $k^2 = [(m^2c^4 - E^2)/c^2\hbar^2]$, Γ is the Lippmann–Johnson operator

$$\Gamma = \mathcal{K} + i\alpha Z\rho_1\sigma \cdot \check{\mathbf{r}}, \tag{18}$$

$\check{\mathbf{r}} = \frac{\mathbf{x}}{r}$, and $\rho_1 \div \rho_3$, $\sigma_1 \div \sigma_3$ are the 4×4 matrices defined in Ref. [32]. Instead of the eigenvalue κ for $\mathcal{K}$ one now has to use $\gamma\kappa$, so that, upon diagonalization, $\Gamma(\Gamma+1) = l(\gamma\kappa)(l(\gamma\kappa)+1)$ and

$$l(\gamma\kappa) = \begin{cases} \gamma\kappa = \left|\kappa^2 - (\alpha Z)^2\right|^{1/2} & \text{for } \gamma\kappa > 0, \\ |\gamma\kappa| - 1 = \left|\kappa^2 - (\alpha Z)^2\right|^{1/2} - 1 & \text{for } \gamma\kappa < 0. \end{cases} \tag{19}$$

Mathematically, Eqs. (16) and (17) look almost the same, and in fact their solution can be reconstructed from the solution of the radial eigenvalue, Eq. (12), discussed in any book on quantum mechanics. Details are given in Appendix A.

The difference between these equations lies only in redefining the parameter l. In the non-relativistic case the combination $l(\kappa)(l(\kappa)+1)$ is the same as $l(l+1)$ as required, while in the relativistic case we should replace l by $l(\gamma\kappa)$. By replacing l in Eq. (12) by $l(\gamma\kappa)$ it is immediately clear that the Madelung rule in its canonical formulation is no longer valid.

4. New physics behind the Madelung rule anomalies

4.1 *The Madelung rule and its anomalies explained with help of Schrödinger's work on the Dirac electron in a gravitational field*

In 1932, the paper by Schrödinger [15] on the Dirac electron in a gravitational field was published. Historically, Dirac [32] came up with his equation in 1928, driven by the observation that the Schrödinger equation is not Lorentz invariant. By correcting this deficiency Dirac uncovered the spin of the electron. In 1927 the spin was artificially inserted into Schrödinger's equation by Pauli. Schrödinger immediately got interested in Dirac's equation and wanted to study how Dirac's formalism might be affected by gravity. The rationale for doing so is given in Schrödinger's paper. The modern viewpoint is presented below. In this subsection we discuss Schrödinger's results in the light of their relevance to the description of the Madelung rule and its exceptions in view of the relevance of Volker Perlick's work [27] on the generalized Bertrand theorem to spectral problems of atomic physics. In [3], the generalized Bertrand theorem was used to derive the regular Madelung rule. To explain the exceptions we need to relativize the calculations already presented. This process was initiated in Sect. 3 and Appendix A.

We begin with the Dirac equation,

$$i\gamma^a \partial_a \psi - m\psi = 0, \tag{20a}$$

in which the Dirac gamma matrices γ^a obey the Clifford algebra anticommutation rule $\gamma^a\gamma^b + \gamma^b\gamma^a = 2\eta^{ab}$, $a, b = 1 \div 4$, where η^{ab} is the matrix enforcing the Minkowski spacetime signature $\{1, -1, -1, -1\}$. As is well known, the equivalence principle of general relativity locally allows the elimination of the effects of gravity (e.g., recall the falling elevator gedanken experiment). Mathematically, this can be achieved by the introduction of the vierbein $e^a_\mu(x)$ so that $e^a_\mu(x)e^b_\nu(x)\eta_{ab} = g_{\mu\nu}(x)$ and $e^\mu_a(x)e^\nu_b(x)g_{\mu\nu} = \eta_{ab}(x)$. Thus, the vierbeins carry in themselves the effects of gravity since the metric tensor $g_{\mu\nu}(x)$ carries the information about gravity.

Introducing these effects into Eq. (20a) can be done as follows. First, the anticommutator $\gamma^a\gamma^b + \gamma^b\gamma^a = 2\eta^{ab}$ is replaced by $\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}$ with the help of the relationship $\gamma^\mu = e^\mu_a\gamma^a$. Here, the Greek indices μ and ν refer to the four-dimensional spacetime, while the Latin indices a, b refer to the Lorentzian (more generally, to the Poincaré) frames. The Lorentzian frames are used to describe rotations in the four-dimensional spacetime of special relativity, while the Poincaré frames account for translations in addition. The partial derivative ∂_μ is now replaced by the covariant derivative

$$\nabla_\mu \psi = \partial_\mu \psi + \Gamma_\mu \psi, \tag{21}$$

where

$$\Gamma_\mu(x) = -\frac{i}{4}\omega_{ab\mu}(x)\sigma^{ab}, \qquad \sigma^{ab} = \frac{i}{2}[\gamma^a, \gamma^b], \tag{22}$$

and

$$\omega^a_{b\mu} = e^a_\nu \partial_\mu e^\nu_b + e^a_\nu e^\rho_b \Gamma^\nu_{\rho\mu}. \tag{23}$$

In the simplest case $\Gamma^\nu_{\rho\mu}$ is the standard Levi-Civita connection determined by the metric tensor $g_{\mu\nu}$. The presence of the term $e^a_\nu \partial_\mu e^\nu_b$ in Eq. (23) is responsible for the torsion effects. These are absent in canonical general relativity. The extension of general relativity accounting for torsion effects is known as Einstein–Cartan gravity [34]. Use of Eq. (21) converts the flat-space Dirac Eq. (20a) into that in the curved space,

$$i\gamma^\mu \nabla_\mu \psi - m\psi = 0. \tag{20b}$$

Instead of Eq. (20b) we can consider the following equation:

$$\begin{aligned} 0 &= (-i\gamma^\mu \nabla_\mu \psi - m\psi)(i\gamma^\nu \nabla_\nu \psi - m\psi) \\ &= \gamma^\mu \gamma^\nu (\nabla_\mu \nabla_\nu + \nabla_\nu \nabla_\mu + \nabla_\mu \nabla_\nu - \nabla_\nu \nabla_\mu + m^2)\psi \\ &= \left(g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \tfrac{1}{8} R_{\alpha\beta\delta\eta}\gamma^\mu \gamma^\nu \gamma^\delta \gamma^\eta\right)\psi, \end{aligned} \tag{20c}$$

where we used the identity [16]

$$\left(\nabla_\alpha \nabla_\beta - \nabla_\beta \nabla_\alpha\right)\psi = \tfrac{1}{8} R_{\alpha\beta\delta\eta}\gamma^\delta \gamma^\eta \psi \tag{24}$$

along with the Clifford algebra anticommutator identity $\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}$. Here, $R_{\alpha\beta\delta\eta}$ is the Riemannian curvature tensor. The above equation can be rearranged further [35], yielding the equivalent final result:

$$\left(g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \frac{R}{4}\right)\psi = 0. \tag{20d}$$

Here, R is the scalar curvature. As demonstrated in Refs. [3,36], the mass term m^2 is not essential and can be eliminated by the appropriate substitutions. In the case of the fish-eye potential this is discussed in Appendix B. Reference [3, Sects. 3 and 5] demonstrates that Eq. (20d) (with $m = 0$) is *exactly equivalent* to Eq. (4). In the mathematical literature such an equation is known as one of the Weitzenbock–Lichnerowicz equations [35,37]; another example is given in Eq. (25) below. Additional information is presented in Appendix E.2.

These types of equations are discussed further below in the context of the Seiberg–Witten theory. The scalar curvature R in Eq. (20d) can be identified with the potential, Eq. (B4) (with $\gamma = 1/2$; see Appendix B). That this chosen scalar curvature coincides with the curvature of the Bertrand space was demonstrated in Ref. [3] and, independently, in Ref. [38]. The obtained result, Eq. (20d), is incomplete, though. To make it complete, following Schrödinger [15] we have to modify the definition of the covariant derivative in Eq. (21). That is, we have to replace $\nabla_\mu = \partial_\mu + \Gamma_\mu$ by $\nabla_{A\mu} = \partial_\mu + \Gamma_\mu - ieA_\mu$, where A_μ is some kind of vector (e.g. electromagnetic) potential. With such a replacement, Eq. (20d) is now replaced by

$$\left(g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \frac{R}{4} + \frac{ie}{2}\sigma^{ab}F(A)_{ab}\right)\psi = 0, \qquad F(A)_{ab} = \partial_a A_b - \partial_b A_a. \tag{25}$$

This is the final result obtained by Schrödinger. In the mathematical literature the same equation is also known as a Lichnerowicz–Weitzenbock equation (more on this is presented in Appendix E.2). Most calculations in S–W theory involve the use of this equation [39]. The signs of the i and e factors in Eq. (25) can be correctly restored. For this, we have to put $\Gamma_\mu = 0$ in

the covariant derivative ∇_μ and then consult a book on quantum electrodynamics, e.g. Ref. [40, Eq. (2.73)].

Equations (16) and (17) can now be related to Eqs. (20d) and (25). Specifically, by setting the fine structure constant α in the Lippmann–Johnson operator to zero we arrive at Eq. (20d). For nonzero α we have to use Eq. (25) instead. Important details are presented below. This kind of logic, common in the physics literature [40], does not take into account finer details, e.g. topological considerations, etc. In the next subsection we initiate the discussion of this topic.

4.2 *The topological transition between Madelung-regular and Madelung-exceptional atoms*

The results just presented now permit us to explain the origins of the Madelung rule exceptions mainly using arguments familiar from the physics literature. This explanation and the results of Appendices E and F will provide an answer to the question of why, for most elements, the relativistic effects are negligible, and why, without exceptions, they are significant for describing atoms exhibiting Madelung rule exceptions. To proceed, it is helpful to make several additional comments:

(i) The term $\frac{ie}{2}\sigma^{ab}F_{ab}$ in Eq. (25) is responsible for the relativistic effects. Without this term, Eq. (25) is converted into Eq. (4) in which $V_{e_\smile}(\mathbf{r})$ is represented by $\frac{R}{4}$. By identifying Eqs. (4) and (21d) we must identify $\frac{R}{4}$ with $V(r)$, Eq. (B4), in which $\gamma = 1/2$.

(ii) The relativistic Eqs. (17) and (25) are equivalent, even though mathematicians prefer to work with Eq. (25) for deep reasons to be explained below.

(iii) The relativistic Eq. (17) and nonrelativistic Eq. (16) look almost the same. Thanks to Ref. [41], these equations can be made to look *exactly* the same (up to the difference in the meaning of the constants in these equations). This is demonstrated in the Appendix A. Because of this circumstance, all the results obtained in Ref. [3] for the nonrelativistic case can now be transferred to the relativistic case unchanged.

(iv) It is of interest to derive the spectrum of the Dirac–Coulomb problem by using the methods developed in Appendix A via replacing the Coulomb potential with the fish-eye potential first, and then by applying the results from Ref. [41]. This is done in Appendices B and C.

In Appendix B we demonstrate the equivalence of the Coulomb and fish-eye classical and quantum problems, while in Appendix C we demonstrate how the hydrogen atom spectrum (both nonrelativistic and relativistic) can be obtained using the fish-eye potential. The treatment of multielectron atoms with help of the deformed fish-eye potential, Eq. (B4), then follows the same steps as outlined in the Appendix C. Additional details are given in Ref. [3].

With this background, following Ref. [40, p. 75], we can now write down the fine structure α expansion for the spectrum of the hydrogen atom ($\hbar = 1$):

$$E_{nj} = mc^2 - \frac{mc^2\alpha^2 Z^2}{2\tilde{n}^2} - \frac{\alpha^4 Z^4 mc^2}{2\tilde{n}^4}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right] + O(\alpha^6). \tag{26}$$

Here, $\tilde{n} = n_r + l + 1$ in accord with results of Appendix C, and $j = \frac{1}{2}, \frac{3}{2}, \ldots, \tilde{n} - \frac{1}{2}$. The α^4 relativistic correction in fact comes directly from the spin–orbital interaction [40, pp. 73–75]. Since this fact is well known but of fundamental importance for this paper, it will be discussed in detail below within the context of S–W theory. In the meantime, by using the deformed fish-

eye potential, Eq. (B4) ($\gamma = 1/2$), and, by repeating the calculations described in Appendices B and C using this deformed potential, the limit $\alpha = 0$ is obtained.

To achieve it requires replacing $\tilde{n}$ by $\tilde{n} + l$ in Eq. (C3), resulting in the regular Madelung rule ($\hbar = 1$):

$$E_{nl} = mc^2 - \frac{me^2Z^2}{2\,(\tilde{n} + l)^2}. \tag{27}$$

For $\alpha \neq 0$ a simple-minded use of the expansion in Eq. (26) in Eq. (27) leads to entirely wrong results. The relativistic effects cannot be neglected for the hydrogen atom, as is well known. They are responsible for the fine structure spectrum. Simple-minded application of the same logic to multielectron atoms then leads us to the conclusion that, based on the methods utilized thus far, the treatment of Madelung-exceptional atoms cannot acquire special status. Either all atoms should obey the standard Madelung rule or they should all be exceptional. The resolution of this paradoxical situation is obtained by providing ramifications to item (ii) above. That is, we now need to explain why mathematicians prefer to work with Eq. (25) instead of Eq. (17). Very deep results in mathematics based on the theory of fiber bundles and spinor bundles (see, e.g., Refs. [37, pp. 152–154] or [35, pp. 40–41]) imply that Eq. (21d) makes sense only for *spin* manifolds. That is, the quantum-mechanical description of atoms exhibiting canonical Madelung-regular behavior should be described exclusively using Eq. (20d).

The relativistic fine structure effects are accounted for with help of Eq. (25). This equation lives on *spin*^{c}-type manifolds [35,37,42]. A description of the transition from atoms obeying the regular Madelung rule to atoms obeying the exceptional Madelung rule cannot be achieved with help of known perturbational methods since it is topological in nature. It is topological since the *spin* and *spin*^{c} manifolds are topologically different. They cannot be smoothly transformed into each other.

This circumstance will be explained in detail below. Before doing so, we would like to explain the difference between the *spin* and *spin*^{c} manifolds using terminology familiar to chemists and physicists. More mathematically rigorous results are presented in the appendices, culminating in Appendix E.4. The differences between these manifolds lie in the differences in the underlying spin symmetry. Topology and symmetry are intertwined, as is well known. More specifically, the results depend upon whether the underlying manifold M is orientable or not. Topologically, this is described in terms of the first Stiefel–Whitney class $w_1(M)$. For an orientable manifold, $w_1(M) = 0$. If, in addition, the manifold can carry the *spin* structure (Appendix D), the second Stiefel–Whitney class $w_2(M)$ should also be zero. This is beautifully explained in Ref. [43, pp. 404–405].

A manifold M which can carry *spin*^{c} is described in terms of the requirement [44, p. 123] $c_1(M) = w_2(M) \bmod 2$. Here, $c_1(M)$ is the first Chern class. For the spin manifolds $w_2(M) = 0$, and this relation breaks down. This explains why *spin* and *spin*^{c} are topologically different manifolds. However, such an explanation does not describe the underlying physics well; this is explained in Appendices E and F. Locally, in language familiar to physicists, it is sufficient to look at the difference between, say, the set of compass arrows (dipoles), emphasizing the orientability of the space in which they live, and the set of nematic molecules (dipoles without charges at the ends), emphasizing the nonorientability of the projective spaces which they supposedly illustrate. It is instructive to check whether such a simplified physical description can be used to visualize *spin* and *spin*^{c} structures. In Appendix F we check whether such a simplified descrip-

tion of the *spin* and *spin*^{c} structures makes sense when applied to Madelung-exceptional atoms. Such a simplified treatment should be considered only as qualitative/nonrigorous; a rigorous treatment in presented in Appendix E.

With these remarks behind us, we still have to demonstrate the equivalence of Eqs. (17) and (25) in order to demonstrate that the relativistic corrections come (in part) from the spin–orbital interactions. The ramifications of such a demonstration will link the Hund rule, the LS, JJ, and LSJ coupling schemes, to the *spin* $\rightleftarrows$ *spin*^{c} topological transition. Following Ref. [40, p. 74], without loss of generality we have, for the centrally symmetric Coulombic field,

$$\frac{ie}{2}\sigma^{ab}F_{ab} = \pm ie\sigma\cdot\mathbf{E} = \pm iZ\alpha\frac{\sigma\cdot\check{\mathbf{r}}}{r^2}, \tag{28}$$

where $\check{\mathbf{r}}$ is a unit vector. A quick look at Eqs. (17) and (18) allows us to realize that the result just obtained enters into the Lippman–Johnson operator, Eq. (18). Thus, at least for the case of a single electron, Eqs. (17) and (25) do coincide. And if this is so, by applying the Foldy–Wouthuysen transformation to Eq. (17) we obtain, in the first order in α, the spin–orbit coupling interaction term [40, pp. 69–75]. This means that Eq. (17) contains information on spin–orbit coupling *to all orders in* α, and therefore spares us from adding the spin–orbital correction to the nonrelativistic Hamiltonian. The situation with this term becomes more complicated for multielectron atoms; detailed calculations are presented in Refs. [45,46].

These papers, and the references therein, indicate that, very fortunately, the complicated expressions can be squeezed back into the known spin–orbital interaction Hamiltonian for the hydrogen atom with an appropriately redefined coupling constant to be determined experimentally. This fact does not affect the analytical structure of Eq. (17), and therefore the exact mapping from the relativistic to the nonrelativitic case described in Appendix A remains intact. Since the spin–orbit interaction Hamiltonian is a first order in α result, it surely cannot compete with the topological arguments in Refs. [37, pp. 152–154] or [35, pp. 40–41] that are valid to all orders in α. These facts, and those in Appendix F, explain the nature of the Madelung rule anomalies at the physical level of rigor.

5. Using Seiberg–Witten theory to explain the normal to superconducting topological transition at the atomic level

In Sect. 1.1 we noticed that the diamagnetic properties of the hydrogen atom make it a superconductor at the atomic level. None of other hydrogen-like atoms, e.g. Li, Na, K, Rb, or Cs, are diamagnetic. In fact, they are all paramagnetic. At the same time, not at all surprisingly, all noble gases are diamagnetic. The hypothesis by Ashcroft and Ginzburg about hydrogen superconductivity raises the following questions:

(i) If atomic hydrogen is a superconductor (since it is subject to the Meissner effect), can we call the noble gases superconductors?
(ii) If condensed and solidified, will all these elements become superconducting?
(iii) Under appropriate pressure–temperature conditions, will all these elements become at least conductors?
(iv) Are there properties, other than zero resistivity, that indicate that a given solid is a superconductor?

Some answers to questions (i)–(iii) can be found in Ref. [5]. As for question (iv), we would like to mention the following. Historically, Madelung-exceptional palladium is the first element

allowing us to find an answer to question (iv). In Sect. 1.2 we stated that Pd is not a superconductor but PdH_x is. Here, as in Sect. 1.2, we are talking first about PdH_x under ambient pressure.

Negligibly small amounts of absorbed hydrogen make palladium superconducting, and its T_c rises directly proportionally to the amount of absorbed H. Since the absorption is reversible (that is, it costs zero energy), palladium is a fantastic catalyst and hydrogen storage provider [11]. The property of reversible absorption allows application to solid palladium of the method of quasiaverages developed by Bogoliubov [13,14]. Although this method was eventually applied to many order–disorder phase transitions, it was initially applied to BCS superconductors. The method of quasiaverages explains why the superconducting condensate is not number conserving. That is, the number of Cooper pairs in the superconducting condensate is not conserved. Below, we argue that (a) all Madelung-exceptional atoms are superconductors in the sense of the conventional mathematical description of superconductivity using either the Ginzburg–Landau framework or the more sophisticated Seiberg–Witten theory, and (b) this property at the level of individual atoms survives solidification due to experimentally observed reversible absorption, the quality shared by all Madelung-exceptional elements [11].

To demonstrate (a), it is instructive to first reconsider the equivalence between Eqs. (17) and (25). Thus far we have used plausible arguments following Ref. [40, p. 74]. These plausible arguments can be made rigorous using results of the S–W formalism. For the sake of space, we expect our readers to have some familiarity with this formalism, at least at the level of Refs. [37,42]. To expedite matters, we also recommend reading at least the first couple of pages of the review in Ref. [40].

For our first step, i.e. to restore Eq. (28) using the S–W equations, we shall follow Refs. [42,47]. Using these, it is sufficient to consider these equations in the flat Minkowski spacetime $\mathbf{R}^{1,3}$. In such a case the covariant derivative $\nabla_{A\mu} = \partial_\mu + \Gamma_\mu - ieA_\mu$ should have $\Gamma_\mu = 0$. For compatibility with Refs. [42,47] we rewrite ∇_μ as $\nabla_\mu = \partial_\mu + A_\mu$. Then, the first of the S–W equations can be written as

$$\gamma^\mu \nabla_{A\mu} \psi = 0. \tag{29}$$

To write the second S–W equation, it is essential to keep in mind the origin of these equations. At first look, it appears that it is sufficient to consult Refs. [37] or [17]. From both sources the S–W equations emerge as generalizations of the Ginzburg–Landau (G–L) equations of superconductivity. Thus, the solutions of the S–W equations must contain vortices/monopoles, typical solutions of the G–L equations. At the very advanced level, this fact was reconfirmed in Ref. [48]. In the present case, our Eq. (25), although included in the S–W formalism, requires some additional explanation. This is presented in Appendix E, thus making our atomic physics problem an intrinsic part of the S–W formalism.

At the same time, the treatment of the G–L equations typically begins with writing the G–L functional whose variation produces the set of G–L equations.

Self-duality considerations then allow the calculations to be simplified considerably and the order of these equations to be reduced from two to one. A very detailed exposition of this topic is given in Ref. [49, Chapters 5 and 6]. Such a reduction was first performed in the context of the Yang–Mills fields by Bogomolny, whose methodology was extended to S–W theory, where first-order self-dual equations are also used.

Reference [47] also uses this reduction. The S–W solution thus obtained, even though it reproduces the result, Eq. (28), is not L^2 normalizable. Similar cases of L^2-normalizable solutions are discussed in Ref. [50]. For S–W monopoles on Kähler and symplectic manifolds, a more advanced treatment is presented in Ref. [51], which essentially uses the results of Ref. [48].

With these remarks we return to Eq. (25) without the mass term, which can be eliminated as explained in Refs. [3,36]. Let $\mathcal{D}_A = \gamma^\mu \nabla_{A\mu}$; then, using the massless Eq. (25), we obtain

$$\int\limits_M \left(\mathcal{D}_A^+ \bar{\psi}, \mathcal{D}_A \psi\right) dvol = \int\limits_M \left\{ (\nabla_A^+ \bar{\psi}, \nabla_A \psi)^2 + \frac{R}{4}(\bar{\psi}, \psi) + \frac{1}{2}(F^+(A)\bar{\psi}, \psi) \right\} dvol = 0, \quad (30)$$

where we used the Hermitian scalar product (,) and the self-dual portion of $F(A)$, i.e. $F(A)^+ = \frac{1}{2}(F(A) + *F(A))$. The notion of a *spinor bundle* (Appendix D) allowed us to write $F(A)\psi = F(A)^+\psi$ [52, p. 76]. The result, Eq. (30), should be compared with the standard G–L functional,

$$S_{\text{G–L}}(A, \psi) = \int\limits_M \left\{ (\nabla_A \psi)^2 + \left|F(A)^+\right|^2 + \frac{R}{4}|\psi|^2 + \frac{1}{8}|\psi|^4 \right\} dvol. \quad (31)$$

To make Eqs. (30) and (31) coincide formally, following Ref. [37], we need (a) to write the two-form $F(A)^+$ as $F(A)^+ = F(A)^+_{ij}\gamma^i \wedge \gamma^j$, and (b) to assume that $F(A)^+_{ij} = \frac{1}{4}(\gamma_i \cdot \gamma_j \psi, \psi)$. Here, $\cdot$ represents Clifford multiplication (Appendix D). After that, we formally obtain

$$S_{\text{S–W}}(A, \psi) = \int\limits_M \left\{ (\mathcal{D}_A \psi)^2 + \left|F(A)^+ - \tfrac{1}{4}(\gamma_i \cdot \gamma_j \psi, \psi)\gamma^i \wedge \gamma^j\right|^2 \right\} dvol = S_{\text{G–L}}(A, \psi), \quad (32)$$

leading to the first, Eq. (29), and the second,

$$F(A)^+ = \tfrac{1}{4}(\gamma_i \cdot \gamma_j \psi, \psi)\gamma^i \wedge \gamma^j, \quad (33)$$

of the S–W equations. Such a Bogomolny-type calculation depends on the assumption in Eq. (33) playing a crucial role in the S–W formalism but, thus far, this is not implied by the atomic physics formalism. This deficiency is corrected in Appendix E.

With these results established, it follows from Eq. (31) that in the case when the scalar curvature $R > 0$, the set of S–W equations just defined contains only the trivial solution $\mathbf{A} = 0$, $\psi = 0$. The identity

$$\frac{1}{2}\Delta |\Phi|^2 = (\nabla_A^+ \nabla_A \Phi, \Phi) - (\nabla_A \Phi, \nabla_A \Phi) \quad (34a)$$

implies

$$\frac{1}{2}\Delta |\Phi|^2 \leq (\nabla_A^+ \nabla_A \Phi, \Phi). \quad (34b)$$

Using Eq. (30) in this inequality, we obtain

$$\Delta |\psi|^2 \leq -\frac{R}{2}|\psi|^2 - (F^+(A)\bar{\psi}, \psi). \quad (35a)$$

By comparing Eqs. (30) and (31) we can rewrite the last result as

$$\Delta |\psi|^2 \leq -\frac{R}{2}|\psi|^2 - \frac{1}{4}|\psi|^4. \quad (35b)$$

This result can be integrated. If the boundary conditions are chosen appropriately, such an integration along with use of the Cauchy–Schwartz inequality and normalization of ψ produces

$$\frac{1}{2}\int\limits_M |\psi|^4 dvol \leq -\int\limits_M R|\psi|^2 dvol \leq \int\limits_M R^2 dvol. \quad (36)$$

Following Ref. [37] and using Eqs. (31)–(33), we finally obtain

$$\int_M \left|F(A)^+\right|^2 dvol \leq \int_M \frac{R^2}{4} dvol. \tag{37}$$

Up to extra factor of $\frac{1}{4}$ on the righrt-hand side, this inequality coincides with the inequality in Eq. (3.5) obtained in Ref. [53]. In our case, the inequality obtained should be interpreted differently. The scalar curvature (the product of electron–electron interactions) controls the existence or otherwise of the *spin*^{c} phase since $F(A)^+$ can be used only when such *spin*^{c} structures are topologically permitted. That is, the Madelung anomalies typically cannot occur in atoms with low electron content. This, physically plausible, result can be considerably enhanced using the concept of the moduli space. Very much like in the Yang–Mills case, the S–W functional as well as the S–W equations should be invariant with respect to gauge transformations. In the present case the gauge group $\mathcal{G}$ is made of maps f from M to S^1. Suppose $u \in \mathcal{G}$; then, the gauge transformations of the S–W equations are described by (not to be confused with scalar multiplication)

$$(A, \psi) \longrightarrow (A + 2u^{-1}du, u^{-1}\psi). \tag{38}$$

The moduli space $\mathcal{M}$ is formally defined as a quotient,

$$\mathcal{M} = \text{solutions}/\mathcal{G}. \tag{39}$$

The most relevant for us is the case when $\mathcal{M} = 0$. In such a case the S–W equations possess only a finite number of localized solutions. This fact provides justification for the existence of a finite number of Madelung-anomalous solutions. In Appendix C we outline a different approach to this result. Surprisingly, in the version of S–W theory considered in Ref. [53], the case $\mathcal{M} = 0$ also happens to be the most interesting one. It is associated with the fact that the manifold M possesses an almost complex structure [35, p. 89]. In physical language, this means that the (semi)classical limit of quantum mechanics on such manifolds is well defined because they admit well-defined classical trajectories. This conclusion was reached by Witten [53] in his first original paper on the subject.

Mathematically, the condition $\mathcal{M} = 0$ occurs for manifolds M for which

$$c_1(L^2)^2[\mathrm{M}] = 3\tau[\mathrm{M}] + 2\chi[\mathrm{M}], \qquad 2c(L) = c(L^2). \tag{40}$$

Here, τ[M] is the signature and χ[M] is the Euler characteristic of M, while $c_1(L)$ is the first Chern class of the line bundle L (connected with S^1 for *spin*^{c} manifolds as explained in Appendix D). A connection with the Atiyah–Singer index theorem can be seen directly from Ref. [35, p. 64]. It is associated with the vanishing of the second Chern class $c_2(S_n^+ \otimes L)$[M]. Here, S_n^+ is part of the *spinor bundle* defined in Appendix D. In Appendix E.4 a physically motivated explanation of *spin*^{c} manifolds is given. This is associated with the phenomenon of superconductivity. Such an explanation is plausible since the S–W theory is reducible to the G–L theory whose origins are in superconductivity [17].

6. From Madelung-exceptional atoms to Madelung-exceptional solids

To our knowledge, this work elucidates for the first time the superconducting nature of Madelung-exceptional atoms. Historically, however, the study of superconductivity at small scales has its beginnings in nuclear physics. It was initiated immediately after the development of superconductivity theory in metals and alloys [54,55]. Obviously, for atomic nuclei as much as for the hydrogen atom or Madelung-exceptional atoms, there is no point in talking about

macroscopic evidence of superconductivity. Superconductivity for these systems should be understood in terms of Bogoliubov's quasiaverages, introduced in Sect. 1.2. This means that the breaking of U(1) gauge invariance associated with nonconservation of Cooper pairs is mathematically reflected in the emergence of quasiaverages [13,14]. At the scale of atomic nuclei, superconductive properties should be studied spectroscopically since the U(1) invariance and its violation is related to the electromagnetic field.

By extending this direction of thought, P. W. Anderson formulated the following problem in 1959 [56]. Suppose we have a metallic superconductor. Suppose that we can make a powder from it containing smaller and smaller grains. Then, there will be a grain size such that it will lose its superconducting properties. Notice, though, that such grains are expected to be larger in size than the atomic nuclei. Nevertheless, if in nuclear physics the concept of superconducting nuclei is firmly established spectroscopically, the same must be true for the superconducting grains. The spectroscopy of such granular materials was discussed in great detail in Ref. [57]. Since the spectroscopy works for granular superconductors, it should also work for the Madelung-exceptional atoms. At the same time, when solids are made of such atoms, the reversible hydrogen absorption becomes indicative of Bogoliubov's quasiaverages. Then, it becomes appropriate to talk about superconductivity by applying the concept of quasiaverages to the reversible absorption. To do so requires the Madelung-exceptional metal to be placed in a gaseous hydrogen environment.

Since nuclear excitations are, in fact, excitations of the quark–gluon plasma, nuclear spectroscopy should seamlessly merge with the spectroscopy of hadrons, and hence with excitations of the Yang–Mills fields. Such a line of research was initiated in Refs. [58,59]. This fact allows us to reduce the discussion in this section to the minimum. Also, it is fortunate that some of the methods we are about to discuss have recently found their place in chemistry [60].

In view of the comments just made, and to put things in the correct perspective, we would still like to make several remarks. First, Eqs. (4) and (25) are manifestations of the Weitzenbock formula,

$$\mathcal{D}^2\psi = 0, \qquad \text{where } \mathcal{D}^2 = \nabla^*\nabla + \mathbf{K}. \tag{41}$$

Here, $\mathcal{D}^2$, defined in Eq. (E12), is the Hodge Laplacian. For the *spin* manifolds $\mathbf{K} = \mathcal{R}^S$, implying that we are dealing with Eq. (4), while for the *spin*^{c} manifolds $\mathbf{K} = \mathcal{R}^S + \mathcal{F}^S$; see, e.g., Eq. (E16), and we are dealing with Eq. (25). As explained in Appendix E.4., superconductivity takes place on *spin*^{c} manifolds only.

Second, the Hodge Laplacian, Eq. (41), is just the linearized analog of the respective Hodge-like Laplacian-type equation for the Yang–Mills fields [61]. Thus, nuclear superconductivity excitations are, in fact, also excitations of the Yang–Mills fields. Reference [59] is devoted entirely to the study of the millennium Yang–Mills gap problem; it is hoped that the present work might eventually provide its own contribution to the gap problem.

Following Refs. [58,59], as well as Refs. [62,63], and using Eq. (E20), we begin with the Hamiltonian, $\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{H}}_V$, and replace the matrix element $\mathrm{V}^{(0)}_{\mathbf{k}\mathbf{k}'}$ by the constant $-g$. The resulting Hamiltonian is then given by Ref. [59, Eq. (5.42)], i.e.

$$\hat{\mathrm{H}} = \sum_f 2\varepsilon_f \hat{N}_f - g\sum_f\sum_{f'} \hat{b}^+_f \hat{b}_f, \tag{42}$$

where $\hat{N}_f = \frac{1}{2}(c^+_{f\,+}c_{f\,+} + c^+_{f\,-}c_{f\,-})$, $\hat{b}_f = c_{f\,-}c_{f\,+}$. Here, the operators $c^+_{f\,\sigma}$ and $c_{f\sigma}$, $\sigma = \pm$, obey the usual anticommutation relations for fermions: $\{c_{f\,\sigma}, c^+_{f'\,\sigma'}\} = \delta_{\sigma\sigma'}\delta_{ff'}$. Having

these results defined, it is convenient to introduce the *seniority* operator [62]: $\hat{v}_f = c^+_{f\,+}c_{f\,+} - c^+_{f\,-}c_{f\,-}$. This takes care of the number of unpaired fermions at each level f. By construction, $[\hat{\mathrm{H}}, \hat{N}_f] = [\hat{\mathrm{H}}, \hat{v}_f] = 0$. These commutators permit us to make a subdivision $\hat{\mathrm{H}} = \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2$ and to count configurations beginning with the situation when $g = 0$ since the eigenvalues v_f of the seniority operator $\hat{v}_f$ (0 and σ) remain unaffected by g. In such a case, let $\hat{\mathrm{H}}_1$ describe the states without Cooper pairs, i.e. it describes the Hilbert space sector for which $v_f = \sigma$. Accordingly, $\hat{\mathrm{H}}_2$ is to be associated with the sector for which $v_f = 0$. Such a subdivision produces a remarkable and unexpected result: the matrix elements of $\hat{\mathrm{H}}_2$ are calculated with help of the *bosonic-type* commutation relations. These are:

$$[\hat{b}_f, \hat{N}_{f'}] = \delta_{ff'}b_f, \qquad [\hat{b}_f, \hat{b}^+_f] = \delta_{ff'}(1 - 2\hat{N}_{f'}). \tag{43}$$

Even though these are bosonic commutators, they are nontraditional ones. In the traditional case we would have $[\hat{b}_f, \hat{b}^+_f] = \delta_{ff'}$. To bypass the emerging difficulty is equivalent to solving the eigenvalue problem for the Hamiltonian, Eq. (42). This was done in Ref. [62], but more elegantly in Ref. [63]. The problem was reduced to finding the spectrum of the Richardson–Gaudin one-dimensional spin chain. Its excitation spectrum resembles that for the nonideal Bose gas. Before writing down this spectrum of H, we define Ω_n as the pair degeneracy of the level n, i.e. Ω_n is the number of values of f for which $\varepsilon_f = \varepsilon_n$. Omitting all the details given in Refs. [58,59,62,63], we introduce the function $F(E)$ via

$$F(E) = \sum_n \Omega_n(2\varepsilon_n - E)^{-1} \tag{44}$$

so that the spectrum for just one Cooper pair is obtained graphically using the equation $F(E) = g^{-1}$. This equation was initially obtained in Ref. [64]. It paved the way for the development of the BCS theory of superconductivity. To extend this result for many Cooper pairs, Richardson assumed that the wave function for H is made of a symmetrized product of N Cooper pair wave functions so that the total energy of the N pairs is the sum of the respective energies of the N Cooper pairs. This assumption allows us to write the spectrum as

$$F(E_{p_i}) = g_i^{-1}, \quad g_i = g\left[1 + 2g\sum_{j\neq i}^{N}(E_{p_j} - E_{p_i})^{-1}\right]^{-1}; \qquad i = 1, \ldots, N. \tag{45}$$

The results presented serve only to introduce the reader to more complicated problems such as (a) crossover from the atomic limit to the bulk metal, and (b) the effects of finite temperatures. The crossover problem (even including the temperature effects) was discussed in detail in Ref. [57, Sect. 5]. Since this review was published in 2001, we decided to provide up-to-date (2020–2021) results. In Ref. [65] the results of

Ref. [62] were further elaborated. In Refs. [66,67] the results of Ref. [57] were significantly elaborated. In Ref. [68] results on nanoclusters of high-temperature superconductors were reported.

7. Summary and discussion

The study of high-temperature superconductors [5] cannot progress without discoveries of new guiding principles. The purpose of this paper is to supply several

such. These are based on theoretical explanations of several empirical observations, and are (a) the majority of Madelung-exceptional elements yield the highest T_cs to date, and (b) Madelung exceptionality is linked with the property of reversible hydrogen absorption

yielding exceptionally high concentration hydrides of these elements (see Refs. [10,11] and Ref. [69, pp. 79–84]). Madelung-exceptional elements have been in use until now without emphasis on their Madelung exceptionality. Empirically, this exceptionality was noticed due to the unusual property of reversible hydrogen absorption. In this regard the most notable example is palladium. The electronic structure of palladium (Appendix F) makes it a benchmark object of study, and it is not too surprising that it was Pd that was used initially in cold fusion experiments.[8]

The empirical ability to absorb a large amount of hydrogen singled out Madelung-exceptional metals as likely candidates for high-T_c superconductors. The fact that the hydrogen absorption is reversible (under the appropriate experimental conditions [70]) caused us to use Bogoliubov's method of quasiaverages [13,14] associated, in the present case, with Cooper pair nonconservation. This property is characteristic of superconductivity.

As argued in Sect. 6, the phenomenon of superconductivity exists at many scales [71]. When looking at the Madelung-exceptional elements, one should not anticipate all of them to be superconductors in traditional sense without a hydrogen environment. But once such an environment is provided (under appropriate pressure–temperature conditions), they all become superconductors in the traditional sense. This is indeed the case, for example, for Pd. Pd is not a superconductor, but in the presence of a small amount of gaseous hydrogen it becomes superconducting under usual ambient conditions (see Sect. 1.2). Since superconductivity is observed at scales ranging from atomic nuclei to neutron stars [71], it is only natural to search for superconductivity at atomic scales, which is what was done in this paper. It is demonstrated here analytically (by nontrivially solving the quantum many-body problem and invoking some results from S–W theory) that only Madedulng-exceptional atoms possess the superconducting property. This might be detected spectroscopically eventually. By solving exactly the quantum many-body problem at the level of a single atom, we briefly sketched ways of extending the results obtained to atomic clusters by relying on methods developed for superconducting clusters. Since the size of the cluster is an adjustable parameter in these calculations, the problem of crossover, from atomic scales to the scales of bulk metals, was briefly outlined as well. In this regard, Ref. [72] might serve as an excellent point of departure for further studies.

Supplementary data

Supplementary material is available at *PTEPHY* online.

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Appendix A. Mapping the Dirac equation into a Schrödinger-like equation

Following Ref. [41], we employ the system of units in which $c = 1$ and $\hbar = 1$. Then, taking into account that in discussing Eqs. (16) and (17) we introduced the factors $\mathcal{K}$ in the nonrelativistic case and Γ in the relativistic, we argued for the combinations $\mathcal{K}(\mathcal{K}+1) = l(\kappa)(l(\kappa)+1) = l(l+1)$ in the nonrelativistic case and $\Gamma(\Gamma+1) = l(\gamma\kappa)(l(\gamma\kappa)+1)$ in the relativistic. Therefore,

[8] See https://en.wikipedia.org/wiki/Cold_fusion.

Eq. (17) acquires the form

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(\gamma\kappa)(l(\gamma\kappa)+1)}{r^2}+\frac{2ZEe^2}{r}+E^2-m^2\right]R_{N,l(\gamma\kappa)}(r)=0. \tag{A1}$$

The nonrelativistic l is now replaced by the relativistic $\kappa=\pm\left(j+\frac{1}{2}\right)$ and $\gamma\kappa=\pm[\kappa-(Ze^2)^2]$; see Eq. (19). In the case of a discrete spectrum, $m^2-E^2>0$. Therefore, it is convenient to introduce new variables as follows: $\mu=[m^2-E^2]^{1/2}$, $\rho=2\mu r$, and $\omega=4Ze^2E/\mu$. In terms of these variables, Eq. (A1) acquires the standard form of the radial equation for the hydrogen atom:

$$\left[\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho}-\frac{l(\kappa)(l(\kappa)+1)}{\rho^2}+\frac{\omega}{4\rho}-\frac{1}{4}\right]R_{N,l(\gamma\kappa)}(\rho)=0; \tag{A2}$$

see, e.g., Ref. [73, Eq. (16.7)]. This transformation allows us to apply unchanged the methodology developed in Ref. [3] for proving the standard Madelung rule.

Appendix B. Mapping of the Coulombic potential problem into the fish-eye problem: Emergence of conformal invariance

As demonstrated by Schrödinger in his first paper on quantum mechanics, the standard Schrödinger equation

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\varphi=\frac{2m}{\hbar^2}(E-V)\varphi \tag{B1}$$

can be obtained variationally from the Hamilton–Jacobi equation [36]

$$\psi_x^2+\psi_y^2+\psi_z^2=2m(E-V), \tag{B2}$$

where $\psi\rightleftarrows\hbar\ln\varphi$. Next, following Ref. [26], we use the canonical change of variables $\xi=\psi_x$, $\eta=\psi_y$, $\zeta=\psi_z$; $x=\omega_\xi$, $y=\omega_\eta$, $z=\omega_\zeta$ subject to the condition $\psi+\omega=x\xi+y\eta+z\zeta$ in Eq. (B2). When V is the attractive Coulombic potential and such transformations are applied to Eq. (B2), the result is

$$\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\varphi+\beta_n\left(\frac{1}{1+x^2+y^2+z^2}\right)^2\varphi=0, \tag{B3}$$

where $\beta_n=\left(\frac{Ze}{E_n}\right)^2$. the chain of transformations just described converts the eigenvalue problem for Eq. (B1) into the Sturmian problem for Eq. (B3). The Coulombic potential $V_{\rm C}=\frac{\rm const}{r}$ in Eq. (B1) is converted into Maxwell's fish-eye potential $V_{\rm F}=\frac{\rm const'}{1+(r/a)^2}$, $r^2=x^2+y^2+z^2$. Here, a is a constant; in Eq. (B3) we select $a=1$.

The conversion into the Sturmian problem has an additional advantage. It converts Eq. (3) into the conformally invariant Eq. (4) [3]. The use of conformal transformations then allows us to recreate *exactly* the effects of many-body electron–electron interactions (at this stage of our study, formally, without explicit accounting for the spin–spin interactions). These are accommodated into the formalism with help of the results of Sect. 4 and Appendix E. The application of conformal transformations to Eq. (B3) converts Maxwell's fish-eye potential $V_{\rm F}$ into its conformally deformed form:

$$V(r)\equiv V(x,y,z)=-\left(\frac{a}{r}\right)^2\left[\frac{n_0}{(r/a)^{-\gamma}+(r/a)^{\gamma}}\right]^2. \tag{B4}$$

This results in the replacement $V_{\rm eff}=V_{\rm F}$ in Eq. (4) by $V(r)$, Eq. (B4). The details are given in Ref. [3]. The application of scaling analysis, the simplest of conformal transformations, indicates that only two exponents γ are permissible. Using $\gamma=1$ recreates the Coulombic fish-eye

potential for the hydrogen atom. Using $\gamma = 1/2$ recreates the multielectron effects for any multielectron atom. Furthermore, using Eq. (B4) with $\gamma = 1/2$ numerically produces *exactly the same* results as those known for the Hartree–Fock potential. The value of the constant β_n is not affected by the use of conformal transformations. The additional bonus of using $V(r)$, Eq. (B4), comes from the very nontrivial exact conversion of $V(r)$ into the potential obtained by Perlick [27] in his studies of the generalized Bertrand theorem.

Appendix C. Calculation of hydrogen and Madelung-regular atomic spectra, and an alternative explanation of the discreteness of moduli space

Appendix C.1 Calculation of the spectrum

To treat the accidental degeneracy in the spectrum of the hydrogen atom, Fock developed an entirely new method of solving the spectral problem [36] by considering the solution of this problem on S^3. Since Eq. (B3) is not an eigenvalue but the Sturmian problem, we cannot apply the Fock method as such. However, we do apply his idea of replacing the treatment of Eq. (B3) in $\mathbf{R}^3$ by the treatment on S^3 in accord with the results of Sect. 3.3.

By lifting Eq. (B3) to S^3 it is converted to Eq. (11a), in which we have to present $Y_{nlm}(\alpha, \theta, \phi)$ as $\Psi_{nl}(\alpha)\, Y_{lm}(\theta, \varphi)$ so that Eq. (11a) acquires the form

$$\left[\frac{l(l+1)}{\sin^2\alpha} - \frac{\partial^2}{\partial\alpha^2} - 2\cot\alpha\frac{\partial}{\partial\alpha}\right]\Psi_{nl}(\alpha) = I_{nl}\Psi_{nl}(\alpha). \tag{C1}$$

Here, $I_{nl} = -\frac{(Ze)^2}{2|E_n|}$ in the nonrelativistic case. In the relativistic case we have to make the replacement $l \to l(\kappa)$ and write $I_{nl} = \left(\frac{\omega}{4}\right)^2$. All the details are given in Appendix A and must be performed considering that E is describing bound states. Next, we write $x = \cos\alpha$ and, by rewriting $\Psi_{nl}(\alpha)$ in terms of such a variable and representing it in the form $\Psi_{nl}(\alpha) = (1-x^2)^{l/2}F_{nl}(x)$, Eq. (C1) is converted into

$$(1-x^2)\frac{d^2}{dx^2}F_{nl}(x) - (2x+1)x\frac{d}{dx}F_{nl}(x) + [I_{nl} - (l(l+2)]F_{nl}(x) = 0. \tag{C2}$$

This is the equation for the Gegenbauer polynomials. Using this fact, we obtain, after some calculation, $I_{nl} = (n+l+1)^2 - 1 \equiv \tilde{n}^2 - 1$. Now let $\tilde{n} = 2F + 1$. Then, $\tilde{n}^2 - 1 = 4F(F+1)$. Using this information, consider, instead of Eq. (11a) (i.e. Eq. (C1)) the equation $\mathcal{L}^2 Y_{nlm} = (I_{nl} - E)\, Y_{nlm}$, in which E is the fixed parameter. The necessity of doing this is explained in Ref. [3, Sect. 4 and Appendix F]. To determine the value of this parameter we analyze the equation $I_{nl} - E = 4F(F+1)$. By selecting $-E = -1$ we obtain $I_{nl} = (2F+1)^2$, implying

$$\frac{-(Ze)^2}{2\,|E_{nl}|} = \tilde{n}^2 \quad \text{or} \quad E_{nl} = \frac{-(Ze)^2}{2\tilde{n}^2} = \frac{-(Ze)^2}{2(n+l+1)^2} \qquad \text{(Schrödinger spectrum)}. \tag{C3}$$

Here, $n = n_r$ in the standard quantum-mechanical notation. For the Dirac case we also obtain

$$\left(\frac{\omega}{4}\right)^2 = (n_r + l(\gamma\kappa) + 1)^2 \qquad \text{(Dirac spectrum)}, \tag{C4}$$

where ω is defined in Appendix A. The result, Eq. (C4), coincides with Ref. [41, Eq. (3.26)]. By restoring c, $\hbar$, and hence α, and using Eq. (C4), we reobtain the known Dirac spectrum.

The Madelung-regular spectrum emerges as a solution of Eq. (11b). In view of the fact that Eq. (11b) emerges as a modification of Eq. (11a) caused by the change from $\gamma = 1$ to $\gamma = 1/2$ in Eq. (B4), Eq. (C1) changes accordingly. This leads to some changes in Eq. (C2) while keeping $I_{nl} = -\frac{(Ze)^2}{2|E_n|}$ unchanged. Due to the changes in Eq. (C2), the spectrum, i.e. Eq. (C3), also changes, resulting in Eq. (27). The details are given in Ref. [3].

Appendix C.2 Discretness of the moduli space

As follows from the results of Sect. 5, we need to provide evidence that, upon relativization, not all atoms become Madelung exceptional. We would like to achieve this by using the inequality in Eq. (36). In this inequality we choose $M = S^3$. On S^3 we shall use properly normalized spherical eigenfunctions $Y_{n+l,,l}m(\alpha, \theta, \varphi)$ as defined in Eq. (11b); see also Ref. [22]. Accounting for relativistic effects leads to the replacement of the quantum number l by $l(\gamma\kappa)$ as defined in Eq. (A1). Also, instead of $I_{nl} = -\frac{(Ze)^2}{2|E_n|} = \tilde{n}^2$, in view of Eq. (C3) we have to use $(I_{nl})^2$ (for R^2), where now $I_{nl} = (n_r + l(\gamma\kappa) + 1)^2$, in view of Eq. (C4).

Since the area of S^3 is a known constant, the inequality in Eq. (36), is regulated by the charge Z of the atomic nucleus. When the inequality becomes an equality in Eq. (36), it provides a complicated equation for Z whose acceptable solutions should be only in terms of nonnegative integer Zs. It is clear, then, that there could only be a countable number of Zs or no Zs at all. The last case brings us back to the Madelung-regular case which does not require such an inequality. This is so because the result from the Eq. (36) equality will not contain the parameter Z at all, and therefore neither the inequality, Eq. (36), nor the equality originating from Eq. (36) make physical or even mathematical sense when Z is absent. That is, relativistic effects are completely ignored.

Appendix D. Spin structures: Group-theoretical and topological aspects

In Sect. 4.1. the anticommutator relation defining the Clifford algebra was presented. In this and the next appendix we develop the quantum many-body formalism using Clifford algebras. We begin with the following.

Appendix D.1 Vector and spinor representations of Clifford algebras

Let V be some vector space of dimension n over $\mathbf{R}$ and g be some nondegenerate bilinear form on V. The Clifford algebra $Cl(V, g)$ is an associative algebra with unit defined by

$$Cl(V, g) = \frac{T(V)}{I(V, g)}, \tag{D1}$$

where $T(V)$ is the tensor algebra and $I(V, g)$ is the ideal created by $x\otimes x + g(x, x)1$ for all $x \in V$.

If we define a map $x \to c(x)$ such that $x\otimes x + g(x, x)1 \to c(x)\otimes c(x) + g(c(x), c(x))1$, then there is a unique algebra homeomorphism: $Cl(V, g(x)) \to Cl(c(V), g(c(x))$. In such a fashion, in Sect. 4.1 we replaced $\gamma^a\gamma^b + \gamma^b\gamma^a = 2\eta^{ab}$ by $\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}$ so that the c-map is $\gamma^\mu = e^\mu_a\gamma^a$. Clearly, other options for c-maps are also possible.

Now let $(e_1, \ldots, e_n)$ be a g-orthonormal basis of V; then

$$\{e_0 := 1, e_k := e_{i_1}\cdots e_{i_k} \mid 1 \le i_1 < \cdots < i_k \le n;\ 0 \le k \le n\} \tag{D2}$$

is the basis of $Cl(V, g)$ with dimension $\dim Cl(V, g) = 2^n$. There is a canonical isomorphism of vector spaces (as algebras) between the exterior algebra and the Clifford algebra, $\Lambda^*V \longrightarrow Cl(V, g)$, i.e.

$$e_{i_1} \wedge \cdots \wedge e_{i_k} \to e_{i_1}\cdots e_{i_k}. \tag{D3}$$

This fact is compatible with the observation that the ideal $I(V, g = 0)$ in Eq. (D1) converts the Clifford algebra into the Grassmann algebra. Thus, the Clifford algebra is a deformation of the Grassmann algebra. The canonical isomorphism, Eq. (D3), makes it possible (and mathematically even necessary) to replace all Grassmann algebra results in physics literature by those involving the Clifford algebra. More details are presented in Appendix E.

The above isomorphism does not depend on the choice of the basis of V. The anti-automorphism t of $Cl(V, g)$ is defined as $(e_{i_1} \cdots e_{i_k})^t = e_{i_k} \cdots e_{i_1}$ $(= (-1)^{\frac{k(k-1)}{2}} e_{i_1} \cdots e_{i_k})$. Thus, $e_{i_1} \cdots e_{i_k}(e_{i_1} \cdots e_{i_k})^t = 1$ (if k is even) or -1 (if k is odd). Using these definitions we are in a position to define the $Pin(V)$ and $Spin(V)$ groups. Specifically, $Pin(V)$ is the group of elements $a \in Cl(V, g)$ such that

$$Pin(V) : \{a = e_1 \cdots e_k \mid g(e_i, e_i) = 1 \text{ for all } i = 1 \div k\}, \tag{D4a}$$

while

$$Spin(V) : \{a = e_1 \cdots e_{2k} \mid g(e_i, e_i) = 1 \text{ for all } i = 1 \div 2k\}. \tag{D4b}$$

By design, for $Spin(V)$ $aa^t = 1$. Let $\rho(a)v = ava^t$, $v \in V$; then one can construct a surjective homeomorphism $\rho\,(Pin(V)) \to O(V)$, while using $Spin(V)$ results in $\rho\,(Spin(V)) \to SO(V)$. By employing these homeomorphisms it can be demonstrated that the group $Spin(V)$ is *universal double cover* of the group $SO(V)$. Its kernel is determined by the equation $\rho(a)v = v$ for all $v \in V$.

Since in this case $aa^t = 1$, we can rewrite the same equation as $av = va$, producing the kernel (fixed point): $a = \pm 1$. The result obtained allows us to make a further step by defining the $Spin^c(V)$ group. To do so requires some preparation. First, we have to define the complexified Clifford algebra $Cl^{\mathbf{C}}(V) = Cl(V, g) \otimes_{\mathbf{R}} \mathbf{C}$. Second, we have to define the *chirality operator* Γ via

$$\Gamma = i^m e_1 \cdots e_n \in Cl^{\mathbf{C}}(V) \tag{D5}$$

so that $m = n/2$ for n even and $m = (n + 1)/2$ for n odd. Evidently, $\Gamma^2 = 1$ and $\Gamma v = v\Gamma$ for even n, and $\Gamma v = -v\Gamma$ for odd n. That is, Γ is an involution operator. This induces a (somewhat involved) decomposition of $Cl^{\mathbf{C}}(V)$ into $Cl^{\mathbf{C}}(V)^{\pm}$ parts. Third, in the $V \otimes \mathbf{C}$ space we must (a) introduce a subspace W made of vectors

$$\eta_j = \frac{1}{\sqrt{2}}(e_{2j-1} - e_{2j}), \qquad j = 1, \ldots, m, \tag{D6}$$

and (b) extend (to $\mathbf{C}$) the Hermitian scalar product in such a way that

$$\langle \eta_i, \eta_j \rangle_{\mathbf{C}} = 0 \qquad \text{for all } j. \tag{D7}$$

This is done with the purpose of introducing the dual space $\bar{W}$ via

$$\bar{\eta}_j = \frac{1}{\sqrt{2}}(e_{2j-1} + e_{2j}), \qquad j = 1, \ldots, m, \tag{D8}$$

so that, instead of Eq. (D7), we obtain

$$\langle \eta_j, \bar{\eta}_j \rangle_{\mathbf{C}} \equiv \|\eta_j\| \qquad \text{for all } j. \tag{D9}$$

Clearly, Eq. (D9) has a quantum-mechanical meaning to be amplified below.

Definition 1. The spinor space S_n is defined as an exterior algebra $\wedge W$ of V (whose dimension is n).

Let $v = w + \bar{w}$. Then, for all $s \in S_n = \wedge W$, the endomorphism $\mathrm{End}_{\mathbf{C}}(S_n)$ denoted as $\rho(w)$ is defined as

$$\rho(w)s := \sqrt{2}\varepsilon(w)s, \tag{D10a}$$

$$\rho(\bar{w})s := -\sqrt{2}i(\bar{w})s. \tag{D10b}$$

Here, $s = \eta_{j_1} \wedge \cdots \wedge \eta_{j_k}$, $1 \le j_1 < \cdots < j_k \le m$, $\varepsilon(\eta_j)s = \eta_j \wedge \eta_{j_1} \wedge \cdots \wedge \eta_{j_k}$, and

$$i(\bar{\eta}_j)s := \begin{cases} 0 & \text{if } j \neq \{j_1, \ldots, j_k\}, \\ (-1)^{l-1}\, \bar{\eta}_j \wedge \cdots \wedge (\bar{\eta})_l^0 \wedge \cdots \wedge \eta_{j_k} & \text{if } j = j_l. \end{cases} \tag{D11}$$

Here, $(\bar{\eta})_l^0$ denotes the term absent in the exterior product. The operator ρ possesses the group representation property: $\rho(vw) = \rho(v)\rho(w)$. The chirality operator, Γ, when rewritten in terms of η and $\bar{\eta}$, allows us to decompose S_n for even n as

$$S_n = S_n^+ \oplus S_n^-. \tag{D12}$$

Here, S_n^+ and S_n^- are eigenfunctions (half-spinors) of the operator Γ whose eigenvalues are ± 1.

Definition 2. The representation ρ of $Spin(V)$ given by Eqs. (D10a) and (D10b) on the spinor space S_n is called a *spinor representation*. The same, but on S_n^+ and S_n^-, is called a *half-spinor representation*.

A spinor representation is a unitary presentation [35]. It preserves the Hermitian product. Therefore, it is ideally suited for quantum-mechanical calculations.

To extend these results for odd n, it is helpful to know [37] that (a) for $\dim V = 2n$, $Cl^{\mathbf{C}}(V) \simeq \mathbf{C}^{2^n \times 2^n}$, and (b) for $\dim V = 2n+1$, $Cl^{\mathbf{C}}(V) \simeq \mathbf{C}^{2^n \times 2^n} \oplus \mathbf{C}^{2^n \times 2^n}$. With this information, the odd-dimensional space V does not create additional problems. The spinor and half-spinor representations admit unique extension to $Spin^{\mathrm{c}}(V)$.

Definition 3. A group $Spin^{\mathrm{c}}(V)$ is a subgroup of the multiplicative group of units (that is, of elements having an inverse) of $Cl^{\mathbf{C}}(V)$. It is generated as a surjective mapping $Spin(V) \times S^1 \longrightarrow Spin^{\mathrm{c}}(V)$, where S^1 is the unit circle in $\mathbf{C}$. If $a \in Spin(V)$ and $z \in S^1$ then the kernel of this mapping is $az = 1$, implying $a = z^{-1} \in Spin(V) \cap S^1$.

Definition 4. $Spin^{\mathrm{c}}(V)$ is isomorphic to $Spin(V) \times_{\mathbf{Z}_2} S^1$, where the $\mathbf{Z}_2$ action identifies (a, z) with $(-a, -z)$. $Spin^{\mathrm{c}}(V)$ yields a nontrivial double covering $Spin^{\mathrm{c}}(V) \longrightarrow SO(V) \times S^1$.

The physical meaning of $Spin^{\mathrm{c}}(V)$ has never been discussed in the mathematical literature. It is explained in Sect. E.4.

Appendix D.2 Spinor and Clifford bundles

If TM is the tangent bundle of M, the Riemannian metric on M reduces the structure group of TM to $SO(n)$, $n = \dim M$. This fact allows us to design the *associated principal* bundle P over M with fiber $SO(n)$. Such an associated bundle is called a *Clifford bundle* (see below). In general relativity such a bundle is known as a *frame bundle* [34]. The uses of the vierbeins $e_\mu^a(x)$ in Sect. 4.1 reflect just this fact. Spinorial analysis elevates this concept one level above that just described. Specifically, it begins with the following definition.

Definition 5. A *spin structure* on M is synonymous to designing the principal bundle $\tilde{P}$ over M with the fiber $Spin(n)$ (universal double cover of $SO(n)$) for which the quotient of each fiber by the center ± 1 is isomorphic to the frame bundle just defined.

Definition 6. A Riemannian manifold with a fixed spin structure is called a *spin manifold*.

Since the fiber $Spin(n)$ operates on the spinor space S_n, Eq. (D12), and, for even n, also on the half-spinor spaces S_n^+ and S_n^-, it becomes possible to talk about the spinor bundle in this context.

Definition 7. The *spinor bundle* $\mathfrak{S}_n$ is defined as

$$\mathfrak{S}_n = \tilde{P} \times_{Spin(n)} S_n. \tag{D13}$$

This definition is to be contrasted with the definition of a *Clifford bundle*.

Definition 8. The bundles $Cl(P)$ and $Cl^{\mathbf{C}}(P)$ defined as

$$Cl(P) = P \times_{SO(n)} Cl(V), \tag{D14a}$$

$$Cl^{\mathbf{C}}(P) = P \times_{SO(n)} Cl^{\mathbf{C}}(V) \tag{D14b}$$

are called *Clifford bundles*.

From the definition of Clifford bundles it follows that the creation of such bundles does not require *spin* or *spin*$^{\mathrm{c}}$ structures. However, they can exist on such structures as well. This is studied further in the next appendix in the context of Dirac operators. The fundamental issue is: if there is a connection between the Clifford and spinor bundles, what physics does such a connection describe? To answer this question requires the introduction of many nontrivial facts, as described below.

Appendix E. Dirac operators on Clifford and spinor bundles

The purpose of this appendix is to demonstrate that Eq. (25) as obtained by Schrödinger accounts for all quantum many-body effects for the atomic multielectron system. At present, relativistic many-body effects are treated with the help of the relativistically extended Hartree–Fock variational methods [28]. In the nonrelativistic limit the Hartree–Fock calculations end up with the eigenvalue in Eq. (3). It does not obey the superposition principle, though. This happens to be a fundamental problem for the development of the quantum mechanics of many-body systems, as explained in detail in Ref. [74], which calls equations like Eq. (3) *De Broglie-type*.

Reference [74] argues that the formalism of second quantization, essential for the development of quantum field theory, is applicable only to Schödinger-type equations for which the superposition principle holds. This is also explained in Ref. [75, p. 108].

Ignoring the supersposition principle makes the underlying equations formally purely classical. That is, in such equations the Planck constant $\hbar$ can be eliminated by appropriate changes of variables and rescaling. This paradoxical situation is explained in detail in Ref. [36]. To our knowledge, in the physics literature the second quantization method is used in many-fermion theory with or without taking account of the superposition principle [76]. In this work, we strictly follow the philosophy of Ref. [74] since it is in formal accord with the Hodge–de Rham theory whose basics we describe below.

We remind the reader that Hodge–de Rham theory is used thus far in Abelian and non-Abelian gauge field theories, and therefore in the gauge-theoretic formulations of gravity.

Appendix E.1 Clifford algebra versus second quantization

A quick and very informative introduction to the formalism of second quantization is given in Refs. [75,76]. From these, it follows that such a formalism was initially designed to treat the processes involving interactions of light with matter. Since photons (bosons) are relativistic objects, this requires fermions to be treated relativistically as well, i.e. with the help of the Dirac equation. However, many books on second quantization begin with the canonical anticommutation

relations given by

$$\{a_i, a_j^+\} = \delta_{ij}, \qquad \{a_i, a_j\} = 0, \qquad \{a_i^+, a_j^+\} = 0. \tag{E1a}$$

From these relations the relativistic aspects of the second quantization of fermions are not at all apparent! However, following Ref. [77], we can correct this deficiency. This is accomplished by introducing the auxiliary operators $\hat{e}_i = a_i - a_i^+$, $\hat{e}_i^+ = a_i + a_i^+$. Using these operators along with Eq. (E1a), we immediately obtain

$$\{\hat{e}_i, \hat{e}_j\} = -\{\hat{e}_i^+, \hat{e}_j^+\} = -2\delta_{ij}, \{\hat{e}_i, \hat{e}_j^+\} = 0. \tag{E2}$$

A quick look at the commutators following Eq. (20a) allows us to recognize in these anticommutators the already familiar Clifford algebra. This allows us to define the Dirac-like operator $d = \sum_i a_i^+ \nabla_i$ and its adjoint $d^+ = -\sum_i a_i \nabla_i \equiv \delta$.[9] Here, the symbols d and δ are the raising and lowering operators of the Hodge–de Rham theory in which the Hodge Laplacian Δ_{H} acting on differential forms (in atomic physics these are the Slater determinants or their linear combinations) is given by

$$\Delta_{\mathrm{H}} = d\delta + \delta d = (d + \delta)^2 . \tag{E3}$$

Appendix E.2 An assortment of Weitzenbock–Lichnerowicz formulas: Hartree–Fock versus Hodge–de Rham

The transformations $\hat{e}_i = a_i - a_i^+$, $\hat{e}_i^+ = a_i + a_i^+$ of the previous subsection are the simplest case of Bogoliubov's transformations [54, pp. 326–336, 527–537]. They are heavily used in condensed matter and nuclear physics theories. In such theories one typically writes

$$\hat{e}_i = u_i a_i - v_i a_i^+, \hat{e}_i^+ = u_i a_i + v_i a_i^+ \tag{E4}$$

subject to the constraint $u_i^2 + v_i^2 = 1$. In such a case, one again ends up with the anticommutator $\{\hat{e}_i, \hat{e}_j^+\} = \delta_{ij}$; see, e.g., Eq. (E2). In physics this is motivated by the desire to make the transformations in Eq. (E4) canonical in the sense of mechanics and quantum mechanics. In mathematics, in the theory of spinors, the same effect is achieved by selecting either the Clifford or spinor bundle.

Selecting between these bundles leads to an assortment of Weitzenbock–Lichnerowicz (W–L) formulas. We begin by selecting the Clifford bundle. Such a choice and the difference between the Clifford and spinor bundles is nicely explained in Ref. [37, pp. 209–210, 213–218], as well as in Appendix D. This allows us, following Ref. [77], to present in this subsection the condensed-matter-like derivation of the same results. To this end, we select the second quantized Hamiltonian $\hat{\mathrm{H}}$ in the form given in Ref. [54, Eq. (58.63)]:

$$\hat{\mathrm{H}} = \sum_i \mathrm{H}_i a_i^+ a_i - \frac{1}{2} \sum_{i,j,k,l} \mathrm{H}_{ijkl} a_i^+ a_j^+ a_k a_l. \tag{E5}$$

The results obtained allow us to demonstrate that $\hat{\mathrm{H}}$ coincides with the Hodge Laplacian Δ_{H}. Such a demonstration brings the condensed matter and atomic physics results in line with those in the Abelian and non-Abelian gauge field theories.

We begin our demonstration by using Eq. (D3). We write $\theta(I) = e_{i_1} \wedge \cdots \wedge e_{i_k}$, $I = \{1 \le i_1 < \cdots < i_k \le n\}$. Using Eqs. (D10a) and (D10b) it is clear that $a_i^+ \theta(I) \rightleftarrows \varepsilon(e_i)\theta(I)$ and $a_i \theta(I) \rightleftarrows i(e_i)\theta(I)$. From here, it follows [77] that (a) $\sum_i a_i^+ a_i \theta(I) = n\theta(I)$, and (b) if A^* is an operator

[9] In the notation of Ref. [37], and in view of Eqs. (D10a) and (D10b), the same results are written as $d = \varepsilon(\eta_i)\nabla_{e_i}$ and $d^+ = -i(\eta_i)\nabla_{e_i}$. See also the next subsection.

inducing an endomorphism of $\theta(I)$,

$$A^*\theta(I) = \sum_{j=1}^{k}(-1)^j e_{i_1} \wedge \cdots \wedge \left(A^* e_{i_j}\right) \wedge \cdots \wedge e_{i_k}, \tag{E6}$$

then, provided that $A = A_{ij}$ is skew symmetric, $A^* = -\sum_{ij} A_{ij} a_j^+ a_j$.

With these results, and using the definitions of d and d^+, the Hodge Laplacian Δ_{H} acting on $\theta(I)$ can now be presented as

$$\begin{aligned}\Delta_{\mathrm{H}}\theta(I) &= -\sum_{k,l}(a_k^+ a_l \nabla_k \nabla_l + a_l a_k^+ \nabla_l \nabla_k)\theta(I)\\ &= -\sum_{k,l}(\{a_k^+, a_l\}\nabla_k\nabla_l - a_l a_k^+(\nabla_k\nabla_l - \nabla_l\nabla_k))\theta(I)\\ &= \left(-g^{ij}\nabla_i\nabla_j + \bar{R}\right)\theta(I),\end{aligned} \tag{E7}$$

where we used Eq. (24). That is, we took into account (see Eq. (E6)) that $(\nabla_k\nabla_l - \nabla_l\nabla_k)(X) = R(X_k, X_l)(X)$, $R(X_k, X_l) = -\sum_{i,j} R_{ijkl} a_i^+ a_j$. And, in view of the second line of Eq. (E7), it is convenient to define $\bar{R} = -\sum_{i,j,k,l} R_{ijkl} a_i^+ a_j a_k^+ a_l$. Since g^{ij} is typically a diagonal matrix, and since $\sum_i a_i^+ a_i \theta(I) = n\theta(I)$, by comparing Eqs. (E5) and (E7) and taking into account properties (a) and $*$b), the identification follows. This provides us with the first step toward explaining why Eq. (4) correctly describes the multielectron atomic system. The task would be completed should $\bar{R}$ in Eq. (E7) be replaced by the scalar curvature R. This requires more work, leading to the assortment of W–L formulas. In particular, we are now in a position to write down the first W–L formula. Following Ref. [77], the first W–L formula is obtained for the Clifford bundle if we are interested in using Eq. (E7) acting on one-forms. In such a case, using Eq. (E1a) we obtain $a_j a_k^+ = \delta_{jk} - a_k^+ a_j$, which we then use in the definition of $\bar{R}$. That is, we obtain

$$-\sum_{i,j,k,l} R_{ijkl} a_i^+ a_j a_k^+ a_l = \sum_{il} R_{il} a_i^+ a_l - \sum_{i,j,k,l} R_{ijkl} a_i^+ a_k^+ a_j a_l. \tag{E8}$$

Here, R_{il} are the components of the Ricci tensor (see below). The last term in Eq. (E8) naturally produces zero when it is acting on $\theta(I)$ since now it is a one-form. Thus, the first W–L formula reads:

$$\Delta_{\mathrm{H}} = \nabla^*\nabla + Ric, \tag{E9}$$

where $\nabla^*\nabla = -g^{ij}\nabla_i\nabla_j$ and, according to Ref. [78], $Ric = \sum_{il} R_{il} a_i^+ a_l$ represents the Ricci tensor. This formula was obtained on the Clifford bundle in Ref. [37, p. 208] by a slightly different method. The detailed derivation of this result using the formalism of Clifford algebras is given in Ref. [79, p. 48]. In view of the developments presented in Sect. 4, it is appropriate to describe some fine details of those derivations in this subsection.

Definition 9. Following Ref. [80, p. 44], we call the combination $\nabla_k\nabla_l - \nabla_l\nabla_k = R(e_k, e_l)$ the *curvature operator*.

Using this definition, the following theorem can be proven [80, pp. 46–47].

Theorem 1. *Let $x \to c(x)$ be a map as defined in Appendix D.1. Let M be a Riemannian manifold and TM its tangent bundle. Then, for any $X, Y, Z \in TM$,*

$$[R(X, Y), c(Z)] = c(R(X, Y)Z). \tag{E10}$$

Definition 10. Let S be the Clifford bundle and let $K(e_k, e_l)$ be the curvature two-form (the same as $R(e_k, e_l)$) with values in End(S). Let e_i be a local orthogonal frame on TM. The endomorphism

$$\mathbf{K} = \sum_{i<j} c(e_i)c(e_j)K(e_i, e_j) \tag{E11}$$

of S is called the *Clifford contraction* of K. It is frame independent.

Corollary 1. *Let $\mathcal{D} = d + d^+$ be the Dirac operator (also, the de Rham operator [80, p. 51]) on the Clifford bundle S. Then, the Weitzenbock formula is given by*

$$\mathcal{D}^2 = \nabla^*\nabla + \mathbf{K}. \tag{E12}$$

Evidently, Eq. (E9) is a special case of Eq. (E12).

Definition 11. On TM the curvature operator R can also be presented via the equation [80, p. 47]

$$R(e_i, e_j)e_a = \sum_l R_{laij}e_l, \tag{E13}$$

where R_{laij} is the four-component Riemann curvature tensor with respect to the orthogonal frame made from the e_i.

Definition 12. The *Riemann endomorphism* $\mathcal{R}^S$ of the Clifford bundle S is defined as

$$\mathcal{R}^S(X, Y) = \frac{1}{4}\sum_{k,l} c(e_k)c(e_l)\langle R(X, Y)e_k, e_l\rangle. \tag{E14}$$

$\mathcal{R}^S$ plays a central role in the W–L-type calculations. Specifically, by analogy with Eq. (E10) it is also possible to arrive at [80, pp. 47–48]

$$[\mathcal{R}^S(X, Y), c(Z)] = c(R(X, Y)Z). \tag{E15}$$

The importance of this result can be seen from [80, Theorem 3.16]:

Theorem 2. *The curvature two-form* $\mathbf{K}$ *is given by*

$$\mathbf{K} = \mathcal{R}^S + \mathcal{F}^S, \tag{E16}$$

where $\mathcal{F}^S$ is the twisting curvature of S.

In Sect. E.4 we demonstrate that the twisting curvature $\mathcal{F}^S$ possesses the property

$$[\mathcal{F}^S(X, Y), c(Z)] = 0. \tag{E17}$$

We also argue that $\mathcal{F}^S \neq 0$ only for the *spin*^{c} manifolds, and therefore $\mathcal{R}^S$ is related to the scalar curvature R while $\mathcal{F}^S$ is related to the Abelian curvature $F(A)$, Eq. (25).

The other two W–L formulas require [37] uses of spinor bundles instead of Clifford bundles. This can be understood if we equivalently rewrite $\bar{R} = -\sum_{i,j,k,l} R_{ijkl}a_i^+a_ja_k^+a_l$ as [77]

$$\bar{R} = -\frac{1}{16}\sum_{i,j,k,l} R_{ijkl}\left(\hat{e}_i\hat{e}_j - \hat{e}_i^+\hat{e}_j^+\right)\left(\hat{e}_k\hat{e}_l - \hat{e}_k^+\hat{e}_l^+\right) = \frac{R}{4} + \frac{1}{8}\sum_{i,j,k,l} R_{ijkl}\hat{e}_i\hat{e}_j\hat{e}_k^+\hat{e}_l^+. \tag{E18}$$

The final result is obtained with help of the relation $\hat{e}_i\hat{e}_j - \hat{e}_i^+\hat{e}_j^+ = -2(a_i^+a_j + a_ia_j^+)$ and by taking into account the symmetry of the Ricci tensor: $R_{ik} = R_{ki}$, $R_{ik} = R_{ijkj}$. For details, see Ref. [77, pp. 70–71]. In Eq. (E18), R is the scalar curvature. The combination $e_ie_j\bar{e}_k\bar{e}_l$ does not act on $\theta(I)$. Instead, it acts on S_n (defined in Eq. (D12)); the second term in Eq. (E18), when

acting on these forms, produces zero. Thus, the second Weitzenbock–Lichnerovicz formula, associated with Eq. (21d), with $m^2 = 0$, reads

$$\Delta_{\mathrm{H}} = \nabla^*\nabla + \frac{R}{4}. \tag{E19}$$

It is given in Ref. [37, p. 218], where it was derived differently (see also [80, Proposition 3.18]). Equation (4) of the main text is obtained with the help of the second W–L formula, while Eq. (25) is obtained with the help of the third W–L formula. Actually, it should be called the Weitzenbock–Lichnerovicz–Schrödinger formula, e.g. Eq. (25), with $m^2 = 0$. It is presented without proof in Ref. [37, p. 220]. This formula plays a central role in the S–W theory discussed in Sect. 5. To derive this formula requires the concepts of spinor and twisted spinor bundles (for *spin*^{c} manifolds). Even though Eq. (25) enters into the S–W theory [39], we need to demonstrate that the formalism of atomic physics developed in this work is not only compatible with the S–W theory but, in fact, must be looked upon as a special case of this theory. This demonstration is presented below.

Appendix E.3 BCS superconductivity and the Hodge–de Rham theory

In Sect. 5, following Ref. [17], we noticed that the S–W equations emerge as generalizations of the G–L equations of superconductivity. The microscopic theory of superconductivity was initially developed in Ref. [78], and independently by Bogoliubov in Ref. [81]. Based on the latter results, Nambu and Jona-Lasinio developed a model of elementary particles whose masses were generated dynamically. This was achieved by superimposing the BCS and Dirac equation formalisms [79]. The detailed derivation of the connection between the BCS and Dirac formalisms is presented in Ref. [55, Problem P.3.2]. Here, we rederive the same results differently for a reason to be explained in the next subsection.

We begin with Bogoliubov's results, following Ref. [82, pp. 755–772] (see also Ref. [83]). We start with the Hamiltonian, Eq. (E5), written in the reciprocal $\mathbf{k}$-space as $\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{H}}_V$. Here, $\hat{\mathrm{H}}_0$ stands for the one-particle Hamiltonian, and V for the potential energy, i.e.

$$\hat{\mathrm{H}}_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}, \qquad \hat{\mathrm{H}}_V = \sum_{\mathbf{k}\mathbf{k}'} V^{(\mathbf{0})}_{\mathbf{k}\mathbf{k}'} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}. \tag{E20}$$

The spin index σ is assumed to have two values, $\uparrow$ and $\downarrow$. In writing $\hat{\mathrm{H}}_V$ only the potential leading to the spin singlet interactions is present since only this potential participates in the superconducting processes. Such an $\hat{\mathrm{H}}$ is the Hartree–Fock-type Hamiltonian [83]. The BCS results now follow from the BCS assumption that

$$\langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle \neq 0. \tag{E21}$$

Here, $\langle \cdots \rangle$ denotes either the quantum-mechanical (zero-temperature) or thermal average. Furthermore, let

$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} V^{(\mathbf{0})}_{\mathbf{k}\mathbf{k}'} \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle. \tag{E22}$$

Then, by applying standard decoupling, the effective interaction Hamiltonian $\hat{\mathrm{H}}^{\mathrm{e}_\smile}_V$ is obtained:

$$\hat{\mathrm{H}}^{\mathrm{e}_\smile}_V = -\sum_{\mathbf{k}} \left(\Delta^*_{\mathbf{k}} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} + \Delta_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} \right). \tag{E23}$$

Bogoliubov's contribution lies in the observations that (a) the anomalous averages, Eq. (E21), lead to nonconservation of the total number of particles (method of quasiaverages [13,14]), and (b) the Hamiltonian $\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{H}}^{\mathrm{e}_\smile}_V$ is a quadratic form made of c-operators obeying the

anticommutation rules in Eq. (E1a). Bogoliubov noticed that such anomalous (quasi)averages are not only typical for superconductivity. They occur in many branches of solid-state physics. They play a pivotal role in this work as well. Use of the method of (quasi)averages results in rigorous *asymptotically exact solutions* of a variety of quantum many-body problems. To deal with problem (b), Bogoliubov proposed diagonalizing the quadratic-form $\hat{\mathrm{H}}$ by introducing new $\gamma_{\mathbf{k}\sigma}$ fermionic operators,

$$\gamma_{\mathbf{k}\uparrow} = u_{\mathbf{k}} c_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c^{\dagger}_{-\mathbf{k}\downarrow}, \qquad \gamma_{\mathbf{k}\downarrow} = u_{\mathbf{k}} c_{\mathbf{k}\downarrow} + v_{\mathbf{k}} c_{-\mathbf{k}\uparrow}, \tag{E24}$$

subject to the standard conditions

$$\{\gamma^{\dagger}_{\mathbf{k}\uparrow}, \gamma_{\mathbf{k}\uparrow}\} = 1, \qquad \{\gamma_{\mathbf{k}\uparrow}, \gamma_{-\mathbf{k}\uparrow}\} = 0, \quad \text{etc.} \tag{E25}$$

The diagonalization of $\hat{\mathrm{H}}$ under such conditions results in the Hamiltonian

$$\hat{\mathrm{H}} = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}} \gamma^{\dagger}_{\mathbf{k}\sigma} \gamma_{\mathbf{k}\sigma}, \qquad E_{\mathbf{k}} = \sqrt{\epsilon_k + |\Delta_{\mathbf{k}}|^2}. \tag{E26}$$

With these results, we are now in a position to rewrite the Hodge–de Rham Laplacian, Eq. (E8), in the form of the Hamiltonian familiar in solid-state physics. From the previous subsection we know that $\sum_i a^{+}_i a_i \theta(I) = n\theta(I)$. Therefore, we are dealing with a Hamiltonian H of the type

$$\sim \mathrm{H} = \sum_{ij} \left[\tilde{g}^{ij} \nabla_i \nabla_j a^{+}_i a_j - R_{ij} a^{+}_i a_j\right], \tag{E27}$$

where $\tilde{g}^{ij} = \frac{1}{n} g^{ij}$. This is a quadratic form for a operators. It can be diagonalized. Upon diagonalization the result will look like that in Eq. (E26), except that $\tilde{E}_{\mathbf{k}} \neq E_{\mathbf{k}}$. The question arises of under what conditions $\tilde{E}_{\mathbf{k}}$ will look the same as $E_{\mathbf{k}}$? This can be achieved based on some auxiliary information from the theory of Dirac operators.

In physics textbooks the operators a^{+}_i, a_j represent the creation and annihilation operators for electrons, while b^{+}_i, b_j are the creation and annihilation operators for positrons (holes). At first look, using these operators in the present context looks permissible but artificial. In the next subsection we demonstrate how this artificiality disappears for the *spin*^{c} manifolds. For the time being, we take care of the positron operators in the usual way,

$$\{b_i, b^{+}_j\} = \delta_{ij}, \qquad \{b_i, b_j\} = 0, \qquad \{b^{+}_i, b^{+}_j\} = 0, \tag{E1b}$$

and impose the additional anticommutator relations

$$\{a_i, b_j\} = \{a_i, b^{+}_j\} = \{a^{+}_i, b_j\} = \{a^{+}_i, b^{+}_j\} = 0. \tag{E1c}$$

Next, we assume that the metric $\tilde{g}^{ij}$ in Eq. (E27) is diagonal, and write, instead of Eq. (E27),

$$\sim \mathrm{H} = \sum_i \left[\epsilon_i a^{+}_i a_i - \epsilon_i b^{+}_i b_i\right] - \sum_{ij} \left[R_{ij} a^{+}_i b_j + R_{ij} b^{+}_i a_j\right]. \tag{E28}$$

In writing Eq. (E28) we assumed that only interactions between particles and holes are nonzero. In the language of solid-state physics, particles are fermions above the Fermi surface while holes are fermions below the Fermi surface.

Taking into account the anticommutation relations, Eqs. (E1a)– (E1c), it is clear that the quantum system as a whole totally decouples so that it is sufficient to consider the diagonalization of the matrix

$$M = \begin{pmatrix} \epsilon & -R \\ -R & -\epsilon \end{pmatrix}, \tag{E29}$$

resulting in the eigenvalues $E = \pm\sqrt{\epsilon^2 + R^2}$ which coincide with those in Eq. (E26). The result obtained is in agreement with Ref. [79], and demonstrates that Bogoliubov's method of quasiaverages [13,14], which results in obtaining asymptotically exact diagonalizable model Hamiltonians, can be translated into the formalism of Hodge–de Rham theory. It remains to demonstrate that the introduction of the positron operators is fully compatible with the third W–L formula, e.g. Eq. (25), playing the central role in S–W theory [39].

Appendix E.4 BCS superconductivity and S–W theory: The physics of spin^c *structures*

From the definitions of Clifford and spinor bundles, Eqs. (D13), (D14a), and (D14b), it follows that the differences between these bundles are the same as the differences between the Lie algebras $so(n)$ and $Spin(n)$ discussed in Appendix D. $Spin(n)$ is a double cover of $so(n)$. Using this fact, it is helpful to restate the content of Eq. (E6) as follows.

Theorem 3 (Lemma 4.8 of [80]). *The Lie algebra $Spin(n)$ can be identified with the vector subspace of $Cl(n)$ spanned by the products e_ie_j, $i \neq j$. The identification associates the antisymmetric matrix A_{ij} with the element $\frac{1}{4}\sum_{i,j} A_{ij}e_ie_j \in Cl(n)$. It can be demonstrated that $A_{ij} = 2(\delta_{i1}\delta_{j2} - \delta_{i2}\delta_{j1})$.*

Using Definition E.3., we notice the following. Let $\{e_k\}$ be a local orthonormal frame for TM. In such a case, the connection and the curvature forms for TM have their values in $so(n)$. In particular, the curvature is the $so(n)$-valued two-form whose matrix entries are (Re_k, e_l), where R is the Riemann curvature operator, e.g. see Eq. (E13).

With help of Theorem E.8, we now obtain

$$\mathbf{K} = \frac{1}{4}\sum\nolimits_{i,j}(Re_k, e_l)e_ie_j \tag{E30}$$

on the Clifford bundle, and

$$\mathbf{K} = \frac{1}{4}\sum\nolimits_{i,j}(Re_k, e_l)c(e_i)c(e_j) \tag{E31}$$

on the spinor bundle. At the same time, using Eqs. (E14), (E16), and (E31) brings us to the conclusion that $\mathbf{K} = \mathcal{R}^S$, implying that $\mathcal{F}^S = 0$.

Corollary 2. *The twisting curvature of the $Spin(n)$ bundle is zero.*

If this is so, we need to demonstrate now that only on $Spin^c(n)$ manifolds does $\mathcal{F}^S \neq 0$. We shall demonstrate this using the physics results obtained in the previous subsection. We begin with the observation that Eq. (E26) an be obtained if and only if the system has positrons (holes) as well as electrons. That is, the system is charged, electrically neutral, and hence Abelian gauge invariant initially.

This observation instantly brings the twisting curvature $\mathcal{F}^S$ into play since, according to Eq. (25), only the twisting curvature is associated with charges. Thus, $Spin^c(n)$ manifolds should be linked with charged systems. Equation (E28) is written for a system of charged fermions. These can be introduced via the set of anticommutators, Eqs. (E1a)–(E1c). Alternatively, instead of using

Clifford algebras with the bilinear form $g(x, y)$ having signature $\{1, \ldots, 1\}$, we can use the bilinear form with signature $\{1, \ldots, 1, -1, \ldots, -1\}$ in which the number of $+1$s is equal to the number of -1s. By analogy with Eqs. (E1a), (E1b), (E1c), and (E2) we introduce the additional

operators $\hat{E}(e_i)$ subject to the Clifford algebra commutation constraint

$$\hat{E}(e_i)\hat{E}(e_j)+\hat{E}(e_j)\hat{E}(e_i)=2\delta_{ij}. \tag{E32}$$

Furthermore, we require that

$$\hat{c}(e_i)\hat{E}(e_j)=\hat{E}(e_j)\hat{c}(e_i),\ \hat{E}(e_j)\equiv E(e_j),$$
$$\hat{c}(e_i)\hat{c}(e_j)+\hat{c}(e_j)\hat{c}(e_i)=-2\delta_{ij},\ \hat{c}(e_i)\equiv c(e_i). \tag{E33}$$

Evidently, the operators $\hat{E}(e_j)$ and $\hat{c}(e_i)$ play exactly the same role as the operators a_i and b_i introduced in Eqs. (E1b) and (E1c). In complete analogy with Eq. (E31), we define the curvature two-form $\mathcal{F}^S$ as

$$\mathcal{F}^S(e_i,e_j)=-\frac{1}{4}\sum\nolimits_{k,l}R_{ijkl}E(e_k)E(e_l). \tag{E34}$$

At the same time, following Ref. [84, pp. 54–55], we rewrite $\mathcal{R}^S$ as

$$\mathcal{R}^S(e_i,e_j)=\frac{1}{4}\sum\nolimits_{k,l}R_{ijkl}c(e_k)c(e_l). \tag{E35}$$

Taking into account Eq. (E16), we now obtain:

$$\begin{aligned}\mathbf{K}&=\mathcal{R}^S(e_i,e_j)+\mathcal{F}^S(e_i,e_j)\\&=\frac{1}{4}\sum\nolimits_{k,l}R_{ijkl}[c(e_k)c(e_l)-E(e_k)E(e_l)]\\&=-\frac{1}{4}\sum\nolimits_{k,l}R_{ijkl}[c(e_k)+E(e_k)][E(e_l)-c(e_l)].\end{aligned} \tag{E36}$$

A quick look at Appendix E.2 allows us to write $c(e_k)\rightleftarrows e_k=a_k-a_k^+$, $E(e_k)\rightleftarrows e_k=a_k+a_k^+$. These results are compatible with the anticommutators in Eqs. (E32) anf (E.33) since Eq. (E1a) was used for the a_k. Thus, we obtain $[c(e_k)+E(e_k)][E(e_l)-c(e_l)]=4a_ka_l^+=-4a_k^+a_l$. Substitution of this result into Eq. (E36) brings us back to Eqs. (E8) and (E9), as required. Moreover, the result obtained is also compatible with Eqs. (E28) and (E29).

We are now in a position to finish the description of $Spin^c(n)$ manifolds. In view of the equivalence $c(e_k)\rightleftarrows e_k=a_k-a_k^+$, and taking into account Eqs. (D10)– (D12), the equivalence just described can also be written as $c(e_k)\rightleftarrows\varepsilon(w)-i(\bar{w})$, while $E(e_k)\rightleftarrows\varepsilon(w)+i(\bar{w})$. The first operator, $c(e_k)$, acts on the W space defined by Eq. (D6), while $E(e_k)$ operates on the $\bar{W}$ space defined by Eq. (D8). Thus, $Spin^c(V)\simeq W\otimes\bar{W}$, in accord with [18, p. 512]. In view of Eq. (D13) this is the spinor bundle (such that, actually, $Spin(V)\times S^1\longrightarrow Spin^c(V)$) in which the associated bundle is made out of elements complex conjugate to that in the principal bundle.

Appendix E.5 Madelung-anomalous superconducting atoms, superconducting density functional theory, and Bogoliubov–de Gennes equations

Superconducting density functional theory (SCDFT) has been very successful in predicting superconductivity for a wide variety of materials, in particular for studying superconductivity in high-pressure environments [5,85]. According to Ref. [86, p. 9], the Bogoliubov–de Gennes (BdG) equations are completely analogous to SCDFT since they are straightforwardly recoverable from SCDFT. According to Ref. [87, Chapter 5], the BdG equations are directly connected with (recoverable from) the equations of the BCS theory of superconductivity. Therefore, it makes sense to provide some details here by connecting general results [5,87] with the results of Appendix E.

We begin with the observation that SCDFT is built around Kohn–Sham (K–S) density functional theory (DFT). Following Ref. [p. 19][5], we notice that the key K–S equation formally

coincides with Eq. (3) of this work. We say "formally" since Eq. (3) is a Hartree–Fock-type equation in which the potential contains the direct and exchange effects [83], while in the K–S equation the potential contains material-independent exchange-correlation effects as well [5]. Nevertheless, using the conformal transformations described in Ref. [3, Sect. 3.3] it is possible to convert Eq. (3), and hence the K–S equation, into an equation looking like our Eq. (4).

But then, according to Appendix E.2, such an equation acquires a geometrical meaning since it can be obtained with help of the second W–L formula. This geometrical meaning is valid for *spin* manifolds only! To obtain Eq. (25) valid for *spin*^{c} manifolds requires much more ingenuity, as explained in Appendix E.4. Surprisingly, only the ingenuity of the purely mathematical results presented in Refs. [80,84] allow us to make a connection with the BdG equations. Using Eq. (29), an eigenvalue equation,

$$\begin{pmatrix} \epsilon & -R \\ -R & -\epsilon \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix}, \tag{E37}$$

is obtained whose eigenvalues are $E = \pm\sqrt{\epsilon^2 + R^2}$. Such an eigenvalue equation coincides exactly with a BdG equation [87, Eq. (5.18)]. Various spacetime-dependent generalizations of Eq. (37) can now be straightforwardly obtained.

Appendix F. *Spin* and *Spin*^{c} structures for Madelung-exceptional atoms: Simplified treatment

In Appendix D, *spin* and *spin*^{c} structures were defined in accord with their definitions in the mathematical literature. In Appendix E.4, the physical interpretation (in terms of superconductivity concepts) of *spin*^{c} structures is given for the first time in the mathematical physics literature. However, it is still of interest to check whether the simple symmetry rules for *spin*^{c} defined in Sect. 4.2 make sense as well. Thus, the purpose of this appendix lies in checking whether the semi-intuitive definitions of Sect. 4.2 work.

For this purpose, the following web link is helpful: https://webelements.com/uranium/atoms.html. Information for other elements can be obtained either by modifying the name in the link or by using the left-hand colunm of the web page, where all the other elements are listed.

Consider, for instance, the spin configuration for the Madelung-regular $_7$N ([He] $2s^2 2p^3$),

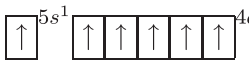
$$\boxed{\uparrow\downarrow}^{1s^2}\ \boxed{\uparrow\downarrow}^{2s^2}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}^{2p^3} \tag{F1}$$

From the web link just given, the 1s and 2s levels are visibly below 2p. Evidently, in the absence of a magnetic field there is spin degeneracy: all "up" spins can be made "down." Not surprisingly, this atom is diamagnetic, just like hydrogen. This is nematic-type degeneracy. But, in addition, there is a permutational symmetry. For $_7$N the electrons at the 2s level are entangled by the Pauli principle. If one of them is "up," the other must be "down." Both can be permuted with electrons at the 2p level where they are all indistinguishable. Such permutations represent the *additional symmetry*.

Whenever there is an additional permutational symmetry the atom is Madelung-regular. Incidentally, Li, Na, Ka, Rb, and Cs are all hydrogen-like and are all paramagnetic, as mentioned in Sect. 1.1. Naively, this observation implies that the "up–down" symmetry is lost, since in the case of H it is manifestly present. This fact is reflected in the periodic table compiled by Madelung [21], who made no comment on this topic. The situation, however, is not as simple as it appears in student textbooks, even those at the advanced level. The standard theory of the

Zeman effect[10] tells us that with respect to the static magnetic field all atoms are both paramagnetic (this is caused by the interaction term linear in the magnetic field, the Pauli paramagnetic term) and diamagnetic (this is caused by the interaction term quadratic in the magnetic field, the Landau diamagnetic term). Experimentally, though, the H atom is strictly diamagnetic while the other hydrogen-like atoms are strictly paramagnetic. Apparently, this fact, and perhaps other factors such as the rigorous development of perturbational theory for superintegrable systems at both classical and quantum levels, resulted in a recent complete recalculation of the results known in the physics literature [1,2,88,89]. The concept of superintegrability is explained in Ref. [3]. References [88,89] do not include perturbations caused by relativistic effects. The sources of these corrections are described in this paper. At the chemical level of rigor part of such a calculation was performed in Ref. [90]. Based on these results, we maintain that for spins the "up–down" symmetry is always present but the magnetic properties of atoms are the result of all kinds of perturbative effects. Therefore, the overall paramagnetism is the cumulative result of these perturbations.

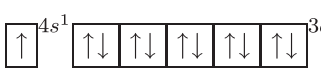
Next, we consider the Madelung-exceptional case, e.g. $_{42}$Mo.[11] If the Madelung-regular rule worked, the filling pattern for Mo would be [Kr] $4d^4 5s^2$. However, experiment yields [Kr] $4d^5 5s^1$:



(F2)

The 4d and 5s levels are not too distant from each other, and furthermore the 4d level is *higher* than 5s! There is an obvious "up–down" symmetry for the 4d level, but since $_{42}$Mo is paramagnetic, the electron on the 5s level should not be mixed with those on 4d. The electron at the *lower* 5s level makes $_{42}$Mo paramagnetic. This (paramagnetic) property can be easily seen by removing all five of the 4d electrons from $_{42}$Mo, resulting in exactly the same electron configuration as rubidium, which is paramagnetic. Nevertheless, as for the other hydrogen-like elements Li, Na, Ka, and Cs, the "up–down" spin symmetry is *not* lost and the paramagnetism is a result of all the corrections mentioned above. The case displayed in Eq. (F1) should be linked with the *spin* manifold because it has permutational symmetry *in addition to* the "up–down" symmetry. The case displayed in Eq. (F2) is linked with the *spin*^{c} manifold because the "up–down" symmetry on the 4d level is manifest.

Exactly the same analysis is applicable to the Madelung-exceptional $_{24}$Cr([Ar] $3d^5 4s^1$) and to its "twin," Nb. In the case of Cr, by stripping it of five electrons sitting on the 3d level, we end up with the configuration of paramagnetic potassium, K. Analogously, for the Madelung-anomalous Nb, if we strip it of four electrons sitting at the 4d level, then we bring the electron configuration to that of paramagnetic rubidium, Rb. The Madelung-exceptional copper, Eq. (F3 a), is diamagnetic, as is gold, since its upper energetic 3d level is occupied by the "Cooper (BCS-type) paired" electrons analogous to the noble gases.[12]



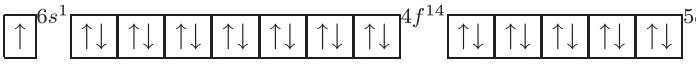
(F3)

[10] See, for example, https://www.damtp.cam.ac.uk/user/tong/aqm/aqmeight.pdf.

[11] For the reader's convenience, a list of all Madelung-exceptional atoms is given at https://en.wikipedia.org/wiki/Aufbau_principle.

[12] And all noble gases are diamagnetic; see https://periodictable.com/Properties/A/MagneticType.html.

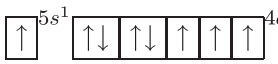
Here, the 4s level is lower than 3d. The pattern for gold is similar:



(F4)

The 5d level has the highest energy and the 6s the lowest.

Analysis of Madelung-exceptional platinum, rodium, and ruthenium proceeds analogously. It is somewhat trickier though. Consider, for instance, ruthenium:



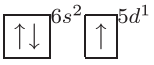
(F5)

Its analysis proceeds in very much the same way as for Mo since, unlike N, whose configuration is displayed in Eq. (F1), all the electron energies at the 4d level are the same. That is, the "Cooper paired" and unpaired electrons are sitting at the same 4d energy level, which is visibly higher than the 5s level.

The treatment of the remaining Madelung-exceptional element palladium remains puzzling. Its electronic configuration apparently implies that it should be diamagnetic, like gold, but it is paramagnetic! Nevertheless, from the point of view of the "up–down" symmetry it is surely

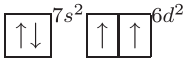
Madelung exceptional.

Next, we want to comment on Madelung-exceptional lanthanides (La and Ce) and actinides (Ac and Th). For $_{57}$La the standard Madelung rule prescribes the configuration [Xe] $4f^1 5d^0 6s^2$, while experiment provides [Xe] $4f^1 5d^1 6s^2$, i.e.



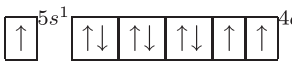
(F6)

As before, level 6s is *lower* than 4f, and this level is lower than 5d. $_{57}$La behaves the same way as the other hydrogen-like atoms and, therefore, is paramagnetic. The electronic configuration of $_{58}$Ce is [Xe] $4f^0 5d^1 6s^2$. It is paramagnetic, as expected, so that its hydrides should have properties very much analogous to those of $_{57}$La. Next, for $_{89}$Ac we have a situation mirroring that of $_{57}$La, except that the orbital energy levels are higher: [Rn] $5f^0 6d^1 7s^2$. Finally, for thorium, $_{90}$Th, we have [Rn] $4f^0 6d^2 7s^2$, i.e.



(F7)

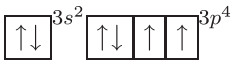
with the 7s energy noticeably lower than the 6d so that, again, we have the *spin*^{c} manifold. We have $_{90}$Th being paramagnetic analogously to all the hydrogen-like atoms. It acts like Madelung-exceptional rhodium, i.e.



(F8)

All lantanides and actinides are paramagnetic, including gadolinium.[13]

Finally, let us take a look at sulfur, S, whose nonmetallic hydride demonstrated the highest T_c to date under high pressures. For $_{16}$S we have



(F9)

which clearly exhibits the "up–down" and permutational symmetries, thus making $_{16}$S Madelung regular and diamagnetic. Two unpaired electrons make $_{16}$S act as if it is Madelung-

[13] See http://mriquestions.com/why-gadolinium.html, though https://periodictable.com/Properties/A/MagneticType.html states that Gd is ferromagnetic.

exceptional $_{90}$Th, thus ensuring its high-temperature superconducting capabilities. These have indeed been observed. The difference in the atomic masses positively affected the observed T_cs.

REFERENCES

[1] A. Rau, Rep. Prog. Phys. **53**, 181 (1990).
[2] H. Friedrich and D. Wintgen, Phys. Rep. **183**, 37 (1989).
[3] A. Kholodenko and L. Kauffman, arXiv:1906.05278 [quant-ph] [Search inSPIRE].
[4] E. Wigner and H. Huntington, J. Chem. Phys. **140**, 764 (1935).
[5] J. Flores-Livas, L. Boeri, A. Sanna, G. Profeta, R. Arita, and M. Eremets, Phys. Rep. **856**, 1 (2020).
[6] J. Gilman, Phys. Rev. Lett. **26**, 546 (1971).
[7] S. Setayandeh, C. Webb, and E. MacA. Gray, Prog. Solid State Chem. **60**, 100265 (2020).
[8] J. Gordon, H. Montgomery, R. Noer, G. Pickett, and R. Tobon, Phys. Rev. **152, 432** (1966).
[9] C. Satterthwaite and L. Toepke, Phys. Rev. Lett. **25**, 741 (1970).
[10] A. Züttel, Mater. Today **6**, 24 (2003).
[11] B. Adams and A. Chen, Mater. Today **14**, 282 (2011).
[12] S. Lundqvist and N. H. March, Theory of the Inhomogeneous Electron Gas(Springer, New York, 2013).
[13] N. Bogoliubov, Lectures on Quantum Statistics, Vol. 2 (Gordon and Breach, New York, 1970).
[14] N. Bogoliubov and N. Bogoliubov, Jr, Introduction to Quantum Statistical Mechanics (World Scientific, Singapore, 2010).
[15] E. Schrödinger, Sitzunsber. Preuss. Acad. Wiss. Phys. Math. **K1**, 105 (1931).
[16] B. Kay, Gen. Rel. Grav. **52**, 1 (2020).
[17] E. Witten, Bull. Am. Math. Soc. **44**, 361 (2007).
[18] L. Nicolaescu, Lectures on the Geometry of Manifolds, 3rd ed. (World Scientific, Singapore, 2021).
[19] P. Thyssen and A. Ceulemans, Shattered Symmetry (Oxford University Press, Oxford, 2017).
[20] H. Bethe and R. Jackiw, Intermediate Quantum Mechanics (CRC Press, New York, 2018).
[21] E. Madelung, Die Mathematischen Hilfsmittel des Physikers (Springer, Berlin, 1936).
[22] M. J. Englefield, Group Theory and the Coulomb Problem (Wiley Interscience, New York, 1972).
[23] Y. Demkov and V. Ostrovsky, Sov. Phys. JETP **13**, 1083 (1971).
[24] H. Goldstein, C. Poole, and J. Safko, Classical Mechanics (Pearson Education Ltd, London, 2014).
[25] M. Gutzviller, Chaos in Classical and Quantum Mechanics (Springer, New York, 2013).
[26] R. Luneburg, Mathematical Theory of Optics (Uuniversity of California Press, Los Angeles, CA, 2021).
[27] V. Perlick, Class. Quant. Grav. **9**, 1009 (1992).
[28] K. Dyall and K. Faegri, Introduction to Relativistic Quantum Chemistry (Oxford University Press, Oxford, 2007).
[29] S. Singer, Linearity, Symmetry and Prediction in the Hydrogen Atom (Springer, Berlin, 2005).
[30] P. Martin and R. Glauber, Phys. Rev. **109**, 1307 (1968).
[31] L. Biedenharn, Found. Phys. **13**, 13 (1983).
[32] P. Dirac, Principles of Quantum Mechanics (Clarendon Press, Oxford, 1958).
[33] P. Collas, Am. J. Phys. **38**, 253 (1978).
[34] F. Hehl, P. Heyede, and G. Kerlick, Rev. Mod. Phys. **48**, 393 (1976).
[35] J. Moore, Lectures on Seiberg–Witten Invariants (Springer, Berlin, 1996).
[36] A. Kholodenko and L. Kauffman, Ann. Phys. **390**, 1 (2018).
[37] J. Jost, Riemannian Geometry and Geometric Analysis (Springer, Berlin, 2005).
[38] S. Kuru, J. Negro, and O. Ragnisco, Phys. Lett. A **381**, 3355 (2017).
[39] S. Donaldson, Bull. Am. Math. Soc. **33**, 45 (1996).
[40] C. Itzykson and J.-B. Zuber, Quantum Field Theory (Dover Publications, New York, 2005).
[41] M. Wong and H.-Y. Yeh, Phys. Rev. D **25**, 3396 (1982).
[42] G. Naber, Topology, Geometry and Gauge Fields: Interactions (Springer, New York, 2013).
[43] M. Nakahara, Geometry, Topology and Physics (IOP Publishing, Bristol, 2003).
[44] L. Nicolaescu, Notes on the Atiyah–Singer Index Theorem (University of Notre Dame, 2013), (available at: https://www3.nd.edu/ lnicolae/ind-thm.pdf, last accessed on January 5, 2022).
[45] M. Blume and R. Watson, Proc. Roy. Soc. (London) A **270**, 127 (1962).
[46] M. Blume, R. Watson, and A. Freeman, Phys. Rev. **134**, 320 (1964).

[47] G. Naber, Geometry, Integrability and Quantization (Coral Press, Sofia, 2000).
[48] C. Taubes, Seiberg–Witten and Gromov Invariants for Symplectic 4-Manifolds (International Press, Somerville, MA, 2010).
[49] A. Kholodenko, Applications of Contact Geometry and Topology in Physics (World Scientific, Singapore, 2013).
[50] C. Adam, B. Muratori, and C. Nash, J. Math. Phys. **41**, 5875 (2000).
[51] A. Sergeev, Vortices and Seiberg-Witten Equations, Lecture Notes (Nagoya University, 2009).
[52] J. Morgan, The Seiberg–Witten Equations and Applications to the Topology of Smooth Four-Manifolds (Princeton University Press, Princeton, NJ, 1996).
[53] E. Witten, Math. Res. Lett. **1**, 769 (1994).
[54] A. Feter and J. Walecka, Quantum Theory of Many-Particle Systems (Dover Publications Inc., New York, 2003).
[55] J.-P. Blaizot and G. Ripka, Quantum Theory of Finite Systems (MIT Press, Cambridge, MA, 1986).
[56] P. Anderson, J. Phys. Chem. Solids **11**, 28 (1959).
[57] J. Non Delft and D. Ralph, Phys. Rep. **345**, 61 (2001).
[58] A. Kholodenko, J. Geom. Phys. **59**, 600 (2009).
[59] A. Kholodenko, Int. J. Geom. Meth. Mod. Phys. **8**, 1355 (2011).
[60] L. Carrier, Ch.-E. Fectau, and P. Johnson, Int. J. Quant. Chem. **120**, 26255 (2020).
[61] D. Freed and K. Uhlenbeck, Instantons and Four-Manifolds (Springer, Berlin, 1984).
[62] R. Richardson and N. Sherman, Nucl. Phys. **62**, 221 (1964).
[63] R. Richardson, J. Math. Phys. **9**, 1327 (1968).
[64] L. Cooper, Phys. Rev. **104**, 1180 (1956).
[65] M. Sambataro and N. Sandulescu, Ann. Phys. **413**, 168061 (2020).
[66] V. Kresin and Yu. Ovchinnikov, Ann. Phys. **417**, 168141 (2020).
[67] N. Kuzmenko, Physica C **576**, 1353709 (2020).
[68] P. Edwards, M. Khojasteh, A. Halder, and V. Kresin, J. Supercond. Nov. Magn. **2021**, 345 (2021).
[69] P. Jena and C. Satterthwaite, Electronic Structure and Properties of Hydrogen in Metals (Plenum Press, New York, 1983).
[70] D. Broom, Hydrogen Storage Materials (Springer Science& Business Media, London, 2011).
[71] D. Dean and M. Hjorth-Jensen, Rev. Mod. Phys. **75**, 607 (2003).
[72] N. Watari, S. Ohnishi, and Y. Ishii, J. Phys. Cond. Matt. **12**, 6799 (2000).
[73] L. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1968).
[74] S. Tomonaga, Quantum Mechanics, Vol. 2, (John Wiley & Sons, Inc., New York, 1966).
[75] S. Tomonaga, The Story of Spin (University of Chicago Press, Chicago, IL, 1997).
[76] F. Harris, H. Monkhorst, and D. Freeman, Algebraic and Diagrammatic Methods in Many-Fermion Theory (Oxford University Press, Oxford, 1992).
[77] S. Rosenberg, The Laplacian on a Riemannian Manifold (Cambridge University Press, Cambridge, 1997).
[78] J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[79] Y. Nambu and G. Jona-Lasinio, Phys. Rev. **122**, 345 (1961).
[80] J. Roe, Elliptic Operators, Topology and Asymptotic Methods (Chapman & Hall/CRC, New York, 2001).
[81] N. Bogoliubov, V. Tolmachev, and1D., A New Method in the Theory of Superconductivity (Consultants Bureau, Inc., Washington, 1959).
[82] C. Henley, Condensed Matter Physics, Lecture 7.3. BCS Theory (Cornell University, 2009).
[83] H. Simon, Lecture Notes for Quantum Matter (Oxford University, 2019).
[84] X. Dai, Lectures on Dirac Operators and Index Theory (University of California, Santa Barbara, 2015).
[85] L. Oliviera, E. Gross, and W. Kohn, Phys. Rev. Lett. **60**, 2340 (1988).
[86] J. Schmidt, C. Benavides-Riveros, and M. Marques, Phys. Rev. B **99**, 224502 (2019).
[87] De Gennes, Superconductivity of Metals and Alloys (CRC Press, Boca Raton, FL, 2018).
[88] F. Fasso, D. Fontanari, and D. Sadovskii, Math. Phys. Anal. Geom. **18**, 30 (2015).
[89] K. Etstathiou and D. Sadovski, Rev. Mod. Phys. **82**, 2099 (2010).
[90] H. Tatewaki, S. Yamamoto, and Y. Hatano, Comp. Theor. Chem. **1125**, 49 (2018).