Searching for High Temperature Superconductivity: From Mendeleev to Seiberg-Witten via Madelung and Beyond
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Recently, a noticeable progress had been achieved in the area of high temperature superconductors. The maximum temperature $T_c$ of 250 K (−230°C) for LaH$_{10}$ and 288 K (+15°C) for CSH$_8$ were reported at the megabar pressures. The highest possible $T'_c$s were achieved by employing hydrides of chemical elements. Empirically, many of these are made of Madelung-exceptional atoms. Here the theoretical background is provided explaining this observation. The, thus far empirical, Madelung rule is controlling 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 some plausible explanation of the role of Madelung-exceptional atoms in the design of high $T'_c$s superconductors. Thus far the atoms obeying the Madelung rule and its exceptions were studied with help of the 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, new methods involve some uses of the Seiberg-Witten (S-W) theory known as the extended Ginzburg-Landau theory of superconductivity. Using results of the S-W theory the difference between the Madelung-regular and Madelung-exceptional atoms is explained in terms of the topological transition. Extension of this, single atom, result to solids of respective elements is also discussed.

Subject index A 13, A 60, A 63, E0
1. Introduction

1.1. Not too widely known facts about the atomic superconductivity

The most essential feature of superconductivity is the Meissner effect—the expulsion of superconductor from the applied static magnetic field. Such 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 will the magnetic properties of individual atoms survive if they form the bulk solid phase. The hydrogen—the simplest of chemical elements—already exhibits a variety of puzzling properties. Although it is studied in every course on quantum mechanics, standard treatments imply that the atomic hydrogen should be both paramagnetic (strongly) and diamagnetic (weakly). In reality, it is diamagnetic only. That is, already the atomic hydrogen is a superconductor!

If this is so, will this property survive for the solid hydrogen? Surprisingly, there is no mathematically rigorous answer to this question.

The standard methods of quantum mechanics indicate that the paramagnetism of hydrogen should exist. 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 but so is Be but they are practically not superconducting in their bulk and Be under normal ambient pressures is very bad superconductor. Thus, bulk superconductivity implies diamagnetism but the opposite is not true. The diamagnetism of atomic hydrogen is a subject matter of hundreds of publications. It can be explained group-theoretically[1], using the theory of quantum chaos [2], or perturbation theory of superintegrable systems.

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

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1 E.g. read the definition of superintegrability in [3]. Study of the sophisticated perturbational theory of superintegrable systems is also mentioned in [3].
a way to reduce the pressures for the hydrogen while retaining superconductivity? The important step in this direction was made by Gilman, in 1971 [6]. He suggested to use hydrides \( \text{XH}_n \), where \( \text{X} \) is an atom other than hydrogen and \( n \) is the number of hydrogen atoms attached to it, perhaps under high pressure. Gilman’s idea to use hydrides instead of hydrogen was named \textit{chemical precompression}.

The idea seemed very attractive because of the following logic behind it. 1) Take an element (metal or not), 2) apply a pressure to it until it becomes a solid, 3) at the stages 1) and/or 2) try to saturate this solid with the atomic hydrogen. Such a saturation will eventually create a hydrogen sublattice inside the host lattice. The sublattice will force 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. 1) How to make an alloy with prescribed number \( n \) of hydrogen atoms? 2) Is there any relationship between \( n \), \( T_c \) and the pressures? 3) How stable are hydrogen sublattices? Since these topics were discussed in [5] this spares us from the extended discussion. At the same time, since answering to these questions brings us directly to the subject matters of this paper we present some additional comments in the next subsection.

1.2. \textbf{Reversible hydrides. Peculiar interplay between the atomic and bulk superconductivities studied with Bogoliubov’s method of quasiaverages}

From the previous subsection we learned that hydrogen—the lightest among atomic superconductors—is expected to yield under very high pressures the highest possible \( T_c \). Even if this result is achieved in laboratory, extremely high pressures make such a project of academic interest only. We do not discuss here situations inside of the 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 #1 from previous subsection still remains. And, hence, some requirements should be applied to make correct selection of the atom \( \text{X} \).

According to [5] (page 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 [5]. At the same time, in [5] the comments on # 2 are as follows (page 5): ”The possibility of predicting \( T_c \) from the first principles played crucial role in the second hydride revolution (dawn of 2000s) as well as the development of computational tools to predict crystal structures and phase diagrams of materials under given thermodynamic conditions.” Nevertheless,
on page 47 of [5] we found the following clarification: "rare-earth and actinides are theoretically challenging to describe, and one can quickly obtain wrong results..." But exactly these elements are the Madelung-exceptional! They are also yielding hydrides with the highest $T'_c$s. This quotation from [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 should be the $T'_c$s is not always working for the following reason. On page 20 of [5] we find: "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 the high $T'_c$s 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 **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 remains as the benchmark model for studying the metal hydrides, beginning with PdH$_x$[7]. For this historical reason, study of superconducting hydrides had began with hydrides of Pd and Th. Incidentally, although both are the Madelung-exceptional, nowhere in the literature this fact is mentioned/emphasized. The motivation thus far came from another observations. Under normal atmospheric pressure Pd is not a superconductor and Th is exceptionally bad superconductor. It has $T_c=1.374 \,^0\text{K}$ [8]. At the same time, the hydride PdH$_{x}$ ($x\simeq 0.7$) is a superconductor, with $T_c \simeq 9\,^0\text{K}$ and for ThH$_{3.84}$ the $T_c$ was found as $8.35\,^0\text{K}$ [9]. These results demonstrate that use of hydrides is step in the right direction. The problem, nevertheless, remains. Yes, the PdH$_x$ and ThH$_{3.84}$ had noticeably improved their $T'_c$s upon making hydrides and, for the PdH$_x$ the $T_c$ is increasing linearly with the linear increase in fraction of H in PdH$_x$ ([5], page 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? Yes, computational advancements formally allow to make predictions of $T'_c$s for the assigned pressure, but to what extent these hydrides can be recreated in real life? And, as it was mentioned above, in this subsection, for the Madelung-exceptional atoms computations are not reliable but the obtained $T'_c$s are among the highest. Because of this we shall focus our attention on Madelung-exceptional atoms. In doing so, we shall cite extensively the content of Ref.s [10],[11].

According to [10], the molecular dissociation of H$_2$ is the first step toward formation of hydrides by absorption. Other than Pd, most metals require energy input in order to overcome the activation barrier. This is achieved by 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 [11] all hydrides for which the absorption is reversible are called **reversible hydrides**. Empirically, it is known [11], page 31, that all the reversible hydrides working 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 keyword: 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 limits of this model. The simplest model of metal is some weakly or strongly interacting electron gas on some jellium-like neutralizing background. It happens, that the description of processes of absorption-desorption based on such model [12] make good sense. Irrespective to ramifications of a given model, all models are subject to some constraints of 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, conservation of particles. These are associated with (global) gauge invariance symmetry. Also, it matters whether particles are bosons or fermions. Photons, phonons, 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 the superconductivity problematics [14]. The concept of quasiaverages is useful whenever there is some change in symmetry. In the present case, we are dealing with the fermion system whose number of particles is not conserved. This is indicative of spontaneous breakage of global U(1) symmetry associated with electromagnetism. Within the framework of superconductivity, details are provided in section 6 and Appendix E.3.

The case of reversible hydrides falls into this category. Indeed, the absorption process begins with \( \text{H}_2 \) breaking into 2 H’s each having proton and electron. Both are fermions. When the pair of H’s enters the bulk solid, it donates 2 electrons (fermions) to the interacting electron gas and 2 protons (fermions) to the jelly. Since the process is reversible, the 2 H’s can emerge back at the surface. Since the bulk system is not particle-conserving such reversible process requires no energy for it to happen. Such picture is missing thus far one very important ingredient. Just described description of absorption-desorption is not at all valid for all solids (metallic or not)! It is only valid for solids made of the hydrides of Madelung-exceptional atoms since already at the atomic level these atoms (and only these!) are superconducting as explained in the Appendices E.4 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 a way just described. This makes sense because Pd is not a superconductor without H’s. Presence of H’s in whatever amounts makes it superconducting in conventional sense. The same is true for other Madelung-exceptional elements. Just presented results allow us to formulate the content

\[5\]
E.g. hydride molecule in the simplest case.
1.3. Organization of the rest of the paper

In section 2 we present basic facts about the atomic physics allowing us to introduce definitions of the Madelung-regular and Madelung-exceptional atoms. In section 3 we initiate an explanation of what makes the Madelung-exceptional atoms exceptional. We argue, that: a) the Madelung-exceptionality is relativistic phenomenon, b) application of relativistic methods known in 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 section 3 we explicitly explain what features make the atoms Madelung-regular. In reading sections 2 and 3 our readers are instructed to read the appendices A, B and C. The reading of these appendices is not optional.

Section 4 is meant to prepare our readers for new information. For this purpose we had converted results of section 3 into equivalent geometrical/topological form allowing us to account for effects of covariance, gauge invariance (local and global), etc. This conversion was influenced by the work of Schrödinger on Dirac electron in the gravitational field. In doing so we used the original work by Schrödinger [30], written in German, as well as its English translation [32]. Results of section 4 allow us to bring into play the results of Seiberg-Witten (S-W) theory in section 5. Although this theory, according to its author, E. Witten [50], is just a sophisticated extension of the Ginzburg-Landau theory of superconductivity, to our knowledge, there were no precedents, till this paper, to demonstrate explicitly (using physical terminology), the connection of the S-W formalism with that for superconductivity. In this work it is done with the purpose of demonstrating that mathematically the transition from the Madelung-regular to Madelung-exceptional atomic behavior is of topological nature. The case of Madelung-regular atoms requires for its description the concept of spin manifold while the Madelung-exceptional atoms can "live" only on spin\(^c\) manifolds. Since the spin\(^c\) and spin manifolds are topologically different, the transition from the Madelung-regular to Madelung-exceptional atoms is topological in nature. The definition of spin\(^c\) manifolds in mathematical literature [70] is devoid of any traces of physics. Being motivated by the physics of reversible hydrides, discussed in subsection 1.2., we found 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 the Appendices D and E.

Finally, in the Appendix F we still further simplified the concept of spin\(^c\) manifolds and tested this simplified definition using known examples of electron filling patterns for the Madelung-exceptional and regular atoms. The S-W formalism also allowed us to demonstrate, in the Appendix C, that the number of Madelung-exceptional elements is always finite and always holds only for heavier atoms, where the relativistic effects are non negligible.

In section 6 we discuss two problems. These are: a) the problem of extension of just obtained single atom results to solids of macroscopic sizes; b) provided that...
the problem a) is solved, will these solids remain superconducting?

Section 7 is devoted to the summary and discussion.

2. Some facts about the periodic system of elements.

Madelung-regular vs Madelung-exceptional atoms

Although quantum mechanical description of multielectron atoms and molecules is considered to be a well developed domain of research, recently published book [15] indicates that there are many topics to be addressed still. The quantum mechanical description of multielectron atom (with atomic number \( Z \) and infinitely heavy nucleus) begins with writing down the stationary Schrödinger equation

\[
\hat{H}\Psi(r_1, r_2, ..., r_Z) = E\Psi(r_1, r_2, ..., r_Z) \tag{1}
\]

with the Hamiltonian

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

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

\[
\hat{H}_i \psi_{\square_i}(r_i) = \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{eff}(r_i)\right)\psi_{\square_i}(r_i) = \varepsilon_{nl}(i)\psi_{\square_i}(r_i), \quad i = 1 \div Z, \tag{3}
\]

where \( V_{eff}(r_i) \) is made of the combined nuclear potential \( -\frac{Ze^2}{r_i} \) and the centrally symmetric Hartree-Fock-type potential \( \mathcal{F}(r_i) \) for the i-th electron coming from the presence of the rest of atomic electrons. The fact that \( \mathcal{F}(r_i) \) is indeed centrally-symmetric was demonstrated in the book by Bethe and Jackiw [16]. It is fundamentally important for our calculations. The symbol \( \square_i \) indicates the i-th entry into 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 hydrogen atom. In quantum many-body system described by Eq.(3) it makes more sense however to associate the concept of an orbital with the description of somehow labeled, say, by interaction with photon (when studied spectroscopically), the i-th electron moving in the centrally symmetric potential \( V_{eff}(r_i) \). The quantum motion in such a potential should cause the hydrogen quantum numbers \( n, l, m \) and \( m_s \) to change into hydrogen-like since the hydrogen atom eigenvalue problem is now being replaced by the eigenvalue problem for the labeled i-th electron in the centrally symmetric potential.

\[\text{e.g. read section 3.3.}\]
$V_{eff}(r_i)$ which is different from the Coulombic. The actual implementation of this observation is presented in this work from the new standpoint. It is known that the number of electrons allowed to sit on such redefined orbital is determined by the Pauli exclusion principle. With increasing $Z$ the electrons are expected to occupy the 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 the atom with $Z$ electrons is made out of atom with $Z-1$ electrons by a) changing the nuclear charge by +1 and, by simultaneously adding one additional electron. In such imaginary process it is assumed that the quantum numbers of electrons in the $Z-1$ atom remain unchanged [17].

The problem with Aufbauprinzip, just described, lies in the assumption that the guiding principle in designing the final ground state electron configuration is made out of two components:

a) knowledge of hydrogen-like wave functions supplying (labeled by) the quantum boxes/numbers $\Box_i$ and,

b) the Pauli principle mathematically restated in the form of fully antisymmetric wavefunction $\Psi(r_1, r_2, ..., r_Z)$. Although mathematically it is just an exterior differential form, the existing treatments do not use the Hodge-De Rham theory of differential forms for description of Pauli principle. In this work this is to be corrected. Should the a) and b) requirements be sufficient, then the familiar hydrogen-like quantum numbers $n, l, m$ and $m_s$ for the hydrogen would make the filling of electronic levels to proceed according to the Fock $n$-rule.

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

This rule leads to problems already for the lithium [15], page 330. As 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 the fixed $N$, the orbitals are filled in order of increasing $n$.

This rule was included by Madelung in his 1936 book[17] in the form of an Appendix 11 describing the filling of periodic table. In the same Appendix 11 Madelung confesses that: a) the filling rule is strictly empirical and, b) as such, it does possesses some exceptions. The Madelung rule and its exceptions require theoretical explanations.

By organizing the elements in periods of constant $n+l$ and, in groups of constant $l, m_l$ and $m_s$, the 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 [15] the period doubling was recreated. Application of the group-theoretic methods to periodic system was done repeatedly in the past. To our knowledge, the most notable results are presented in Chapter 6 of the book by Englefield[18]. Much later, the results of Chapter 6 were independently reobtained in[15]. Should the Madelung rule be without exceptions, just mentioned results would be sufficient. However, the existing exceptions for some transition metals, lanthanides and actinides indicate that uses of the dynamical group theory methods alone are not sufficient. As result, in this work we describe the alternative methods enabling us to explain the Madelung rule and its exceptions.

The problem of finding the theoretical explanation of the Madelung rule had attracted the attention of Demkov and Ostrovsky (D-O)[19]. They used methods, other than group-theoretic, enabling them to guess $V_{eff}(r_i)$ correctly. This had been achieved by taking into account implications of the Bertrand theorem of classical mechanics [20]. It imposes apparently insurmountable restrictions on the selection of $V_{eff}(r_i)$: for spherically symmetric potentials only the Coulombic $-\frac{Ze^2}{r_i}$ and the harmonic oscillator $kr^2$ potentials allow dynamically closed orbits. Theoretical treatment of multielectron atoms before D-O works was confined either to study of spectra of classically and quantum mechanically chaotic systems or to uses of variational (relativistic or not) Hartree-Fock spectral calculations. Beginning with the motion of electrons in helium atom, the classical (and, hence, the semiclassical!) dynamics of electrons in multielectron atoms is believed to be chaotic. The seminal book by Gutzwiller [21] is an excellent introduction to this topic. Already Bethe and Jackiw[16] noticed that the Hartree-Fock $V_{eff}(r_i)$ is centrally symmetric. This brings into question the issue of description of multielectron atom at the semiclassical level. D-O found 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 hydrogen atom. D-O believed that such a replacement might help them to cope with the multielectron effects while keeping an agreement with the Bertrand theorem. To do so, they: a) replaced the Coulomb potential by the fish-eye potential and b) used the conformal transformations applied to the fish-eye potential aimed at conformally deforming this potential in such a way that it will correctly represent 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 the Appendix B we reproduce needed details and comment on some flaws in D-O reasonings. At the quantum level D-O believed that "The Maxwell’s fish-eye problem is closely related to the Coulomb problem.” Being aware of the book by Luneburg [22] D-O nevertheless underestimated the nature of the connection between the Coulombic and optical (fish-eye) problems. The assumption of only "close relationship” caused D-O to replace Eq.(3) by

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{eff}(r_i) \right] \psi(r_i) = 0. \quad (4)$$
Eq.(4) is looking differently from Eq.(3). Eq.(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 $V_{eff}(r_i)$ must be quantized. Such quantization of parameters is making Sturmian and eigenvalue problems equivalent. To prove this equivalence is nontrivial but possible. It was overlooked by D-O. In [3] it is demonstrated that even though Eq.s (3) and (4) are producing exactly the same spectrum, only Eq.(4) can be subjected to the conformal transformations while Eq.(3) cannot. That such transformations will lead to the correct reproduction of the multielectron effects and are complacent with the extended Bertrand theorem is also demonstrated in[3]. The complacency with the Bertrand theorem had become possible only thanks to seminal work by Volker Perlick [23]. In it the results of the classical Bertrand theorem[20] valid in flat Euclidean 3 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 by Perlick. In[3] such a demonstration was performed. Thus, for the first time the place of gravity effects in testable realistic quantum mechanical problem was found\footnote{More accurately, following J.A.Wheeler, we have to use the term ”geometrodynamics” instead of gravity. Recall, that Wheeler’s geometrodynamics is just elaboration on unified theory of gravity and electromagnetism proposed by G.I.Rainich in 1925.}. In addition, in [3] the connection between the deformed D-O potential and the Hartree-Fock $V_{eff}(r_i)$ potential was found. These achievements enable us to make 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 have defined the Madelung rule. The opposite of this definition can be taken as definition of Madelung-exceptions. Ref.[15] leaves us with the impression that the correct mathematical understanding of the empirical Madelung rule can be made only with uses of the results of the dynamical group theory while the D-O results suggest alternative approach which was significantly improved in [3]. If this is so, is there in this formalism a room for description of the Madelung-exceptional elements? From section 1 it follows that the Madelung exceptions are observed among some transition metals, lanthanides and actinides. The electronic structure of these elements was studied thus far with help of the relativistic Hartree-Fock methods [24]. The major new problem emerges: will the results of solving Eq.(4) developed in detail in [3] survive the relativistic extension? Only such an extension may yield the results compatible with that for the Madelung-exceptional atoms. The most difficult issue in doing so is this. Since the already obtained nonrelativistic results are capable of deriving the regular Madelung rule quantum mechanically, the relativization of these results is going to make all...
chemical elements anomalous since the standard \cite{24} formalism works indiscriminantly for all atoms. The Seiberg-Witten (S-W) theory helps to solve this puzzle. This can be achieved in several steps.

**3.2. Preparing the nonrelativistic results for their relativistic extension**

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

$$\hat{H} = p^2 - \frac{2}{r}.$$  \hfill (5)

The Laplace-Runge-Lenz vector $A_0$ is given by

$$A_0 = \frac{x}{r} + \frac{1}{2}(L \times p - p \times L)$$  \hfill (6)

with the angular momentum operator $L$ defined as usual by $L = x \times p$. It is convenient to normalize $A_0$ as follows

$$A = \begin{cases} A_0(-H)^{\frac{1}{2}} & \text{for } E<0, \\ A_0 & \text{for } E=0, \\ A_0 = (H)^{\frac{1}{2}} & \text{for } E>0. \end{cases}$$  \hfill (7)

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

$$J(\alpha) \times J(\alpha) = iJ(\alpha), \alpha = 1, 2,$$

$$[J(1), J(2)] = 0.$$  \hfill (8)

Taking into account that $L \cdot A = 0$ we also obtain two Casimir operators: $L \cdot A = 0 = A \cdot L$ and $L^2 + A^2$. The Lie algebras $J(\alpha) \times J(\alpha) = iJ(\alpha), \alpha = 1, 2$, are the algebras of rigid rotators for which the eigenvalues $j_\alpha(j_\alpha + 1)$ are known from the standard texts on quantum mechanics. The peculiarity of the present case lies in the fact that $J(1)^2 = J(2)^2$. This constraint is leading us to the requirement: $j_\alpha = j_\beta = j$. The topological meaning of this requirement is explained in section 5 of \cite{3}. In short, the eigenvalue equation for the standard quantum mechanical rigid rotator is that for the Laplacian living on a 2-sphere $S^2$. Since in the present case we are having 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 3-sphere $S^3$. Group-theoretically the same result can be restated as $so(4) \simeq so(3) \oplus so(3)$. With such background we are ready to relativize these results.

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3.3. Sketch of derivation of the Madelung-regular rule

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

$$L^2 Y_{lm}^m(\theta, \phi) = l(l + 1)Y_{lm}^m(\theta, \phi).$$

is helpful. Notice, however, that $L^2 = L_x^2 + L_y^2 + L_z^2$ and $L_x = iD_{23}, L_y = iD_{31}, L_z = iD_{12}$,

and $d$ is the dimensionality of space. Let now $A_x = iD_{14}, A_y = iD_{24}, A_z = iD_{34}$. If $L^2$ represents the Laplacian on $S^2$, the combination $L^2 + A^2 \equiv \mathcal{L}^2$ represents the Laplacian on $S^3$ embedded in 4 d Euclidean space[18]. That is, instead of more familiar study of 3-dimensional rigid rotator "living" on the two-sphere $S^2$, the eigenvalue problem for hydrogen atom is in fact involving the study of spectrum of the rigid rotator on $S^3$. This fact was realized initially by Fock [25]. The 3 Euler’s angles $\alpha, \theta, \phi$ on $S^3$ are replacing more familiar $\theta, \phi$ angles used on the 2- sphere. The eigenvalue, Eq.(9), is being replaced now by

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

This result coincides with that obtained in the Appendix C, Eq.(C.1). Here we have the manifestly spherically symmetric wave functions with indices $n, l, m$. This result is immediately applicable to the hydrogen atom [18]. It corresponds to the choice $\gamma = 1$ in Eq.(C5). The choice $\gamma = 1/2$ in the potential, Eq.(B.4), results in the shift in the indices in Eq.(11a) leading to

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

in accord with qualitative arguments made in section 2. In spite of the apparent simplicity of transition from Eq.(11a) to (11b) and with account of 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 the Appendix C, Eq.(C.3). While 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 the position to develop the theory explaining the Madelung-exceptional atoms.

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

This task can be completed in several steps. First, we notice that in the standard 3
dimensional calculations the hydrogen spectrum is determined by the eigenvalues of the radial equation
\[
\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + V(r)\right]R_{E_l}(r) = E R_{E_l}(r).
\]
(12)

Here, the total wave function
\[
\Psi_E = F_{E_l}(r) Y_{l_m}(\theta, \phi), \quad Y_{l_m}(\theta, \phi) = r^l Y_{l_m}^{(\alpha)}(\theta, \phi), \quad R_{E_l}(r) = r^l F_{E_l}(r)
\]
and
\[
V(r) = -\frac{Ze^2}{r}, \quad m = 1, h = 1.
\]

The combination \(F_{E_l}(r) Y_{l_m}(\theta, \phi)\) can be rewritten in terms of \(Y_{nlm}(\alpha, \theta, \phi)\) as demonstrated in [3] in accord with [18]. Therefore, it is sufficient to look at 3 dimensional results. They can always be mapped into \(S^3\) via inverse stereographic projection. Next, this observation allows us, following Martin and Glauber [26] and Biedenharn [27] to use the Pauli matrices \(\sigma_i\) in order to rewrite \(L^2 = (\sigma \cdot L)(\sigma \cdot L + 1)\). This identity permits us then to write the total momentum \(J\) as \(J = L + \frac{1}{2}\). After that, it is convenient to introduce the operator \(K = \sigma \cdot L + 1\) used already by Dirac [28] in his treatment of hydrogen atom with help of the Dirac equation. Using this operator it is possible to obtain the identity:
\[
K^2 = J^2 + \frac{1}{4}, \quad h = 1.
\]

The eigenvalues of \(K\), denoted as \(\kappa\), are known to be \(\kappa = \pm 1, \pm 2, \ldots, 0\) is excluded. Use of these results implies:
\[
l = l(\kappa) = \begin{cases} 
\kappa, & \text{if } \kappa \text{ is positive} \\
|\kappa| - 1, & \text{if } \kappa \text{ is negative}
\end{cases}
\]
\[
j = j(\kappa) = |\kappa| - \frac{1}{2}.
\]
(13)

The above results were presented with purpose not at all discussed in the standard texts on quantum mechanics. Specifically, at the classical level, the Kepler trajectories can be determined with help of the vector \(A\) only [29]. This fact suggests that the quantum analog of \(A\) should produce the 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 \((\mathcal{N})^2 = (\sigma \cdot A)^2 + (K)^2\). Since it can be shown that \(\sigma \cdot A\) and \(K\) anticommute, it becomes also possible to write
\[
\mathcal{N} = \sigma \cdot A + K.
\]
(14)

Denote the eigenvalues of \(\mathcal{N}\) as \(\pm N\). Then, it is possible to demonstrate that
\[
\sigma \cdot A \mid N, \kappa, m > = (N^2 - \kappa^2)^{\frac{1}{2}} \mid N, -\kappa, m >.
\]
(15)

It is possible as well to demonstrate that \(\mathcal{N} \equiv E\) with \(E\) defined in Eq. (12). With help of this result it is possible next to write the exact equivalent of the radial Eq. (12). It is given by
\[
\left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{\mathcal{N}(\mathcal{N} + 1)}{r^2} + \frac{2Ze^2}{r} - \kappa^2\right]F_{N,l(\kappa)}(r) = 0.
\]
(16)
Here $k^2 = 2|E|, m = 1, \hbar = 1$. Biedenharn [27] explains how the wave function $|N, -\kappa, m\rangle$ is related to $F_{N,l(\kappa)}(r)$. Also, $K(K + 1) = l(\kappa)(l(\kappa) + 1)$.

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

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

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{\Gamma(\Gamma + 1)}{r^2} + \frac{2\alpha Z E}{c^2 \hbar r} - k^2 \Phi_{N,l(\gamma \kappa)}(r) = 0. \quad (17)$$

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

$$\Gamma = K + i\alpha Z \rho_1 \sigma \cdot \bar{r}, \quad (18)$$

$\bar{r} = \bar{x} / r, \rho_1 / \rho_3, \sigma_1 / \sigma_3$ are the $4 \times 4$ matrices defined in Dirac’s book [28]. Instead of the eigenvalue $\kappa$ for $K$ now one has to use $\gamma \kappa$ so that, upon diagonalization, $\Gamma(\Gamma + 1) = l(\gamma \kappa)(l(\gamma \kappa) + 1)$ and

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

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

The difference between these equations lies only in redefining the parameter $l$: In the nonrelativistic 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.(12b) 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 Dirac electron in a gravitational field

In 1932 the paper by Schrödinger [30] on Dirac electron in a gravitational field was published. Historically, Dirac [28] came up with his equation in 1928 being driven by the observation that the Schrödinger equation is not Lorentz invariant. By correcting this deficiency Dirac uncovered the spin of electron in 1928. 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. Modern viewpoint will be presented below. In this subsection we discuss Schrödinger’s results in the light of their relevance to the description of Madelung rule and its exceptions in view of the noticed relevance of Volker Perlick’s work [23] on the generalized Bertrand theorem to spectral problems of the atomic physics. In [3], the generalized Bertrand theorem was used for the derivation of the regular Madelung rule. To explain the exceptions we need to relativize the already presented calculations. This process was initiated in section 3 and Appendix A.

We begin with the Dirac equation

$$i\gamma^a \partial_a \psi - m\psi = 0 \quad (20a)$$

in which the Dirac gamma matrices $\gamma^a$ obey the Clifford algebra anticommutation rule $\gamma^a \gamma^b + \gamma^b \gamma^a = 2\eta^{ab}$, $a, b = 1 \div 4$, $\eta^{ab}$ is the matrix enforcing the Minkowski spacetime signature $\{1, -1, -1, -1\}$. As is well known, the equivalence principle of general relativity locally allows to eliminate the effects of gravity (e.g. recall the falling elevator gedanken experiment). Mathematically, this can be achieved by introduction of a vierbein $e^a_\mu(x)$ so that $e^a_\mu(x) e^b_\nu(x) \eta_{ab} = g_{\mu \nu}(x)$ and $e^a_\mu(x) e^b_\nu(x) g_{\mu \nu} = \eta_{ab}(x)$. 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 help of the relationship $\gamma^\mu = e^a_\mu \gamma^a$. Here the Greek indices $\mu$ and $\nu$ refer to the 4-dimensional spacetime while the Latin indices $a, b$ are referring to the Lorentzian (more generally, to the Poincaré’ frames) frames. The Lorentzian frames are used for description of rotations in 4 dimensional spacetime of special relativity while the Poincaré’ frames account for translations in addition. The partial derivative $\partial_\mu$ is replaced now by the covariant derivative

$$\nabla_\mu \psi = \partial_\mu \psi + \Gamma_\mu \psi, \quad (21)$$

where

$$\Gamma_\mu(x) = -\frac{i}{4} \omega_{ab\mu}(x) \sigma^{ab} ; \sigma^{ab} = \frac{i}{2} [\gamma^a, \gamma^b] \quad (22)$$
and
\[ \omega_{b\mu}^{a} = e_{a}^{\nu} \partial_{\mu} e_{b}^{\nu} + e_{a}^{\nu} e_{b}^{\nu} \Gamma_{\rho \mu}^{\nu}. \] (23)

In the simplest case \( \Gamma_{\rho \mu}^{\nu} \) is the standard Levi-Civita connection determined by the metric tensor \( g_{\mu \nu} \). Presence of the term \( e_{a}^{\nu} \partial_{\mu} e_{b}^{\nu} \) in Eq.(23) is responsible for the torsion effects. These are absent in the canonical general relativity. Extension of general relativity accounting for the torsion effects is known as the Einstein-Cartan (ECG) gravity [31]. Use of Eq.(21) converts the flat space Dirac Eq.(20a) into that in the curved space
\[ i \gamma^{\mu} \nabla_{\mu} \psi - m \psi = 0. \] (20b)

Instead of Eq.(20b) we can consider the following equation:
\[
0 = (-i \gamma^{\mu} \nabla_{\mu} \psi - m \psi)(i \gamma^{\nu} \nabla_{\nu} \psi - m \psi)
= \gamma^{\mu} \gamma^{\nu}(\nabla_{\mu} \nabla_{\nu} + \nabla_{\nu} \nabla_{\mu} + \nabla_{\mu} \nabla_{\nu} - \nabla_{\nu} \nabla_{\mu} + m^{2}) \psi
= (g^{\mu \nu} \nabla_{\mu} \nabla_{\nu} + m^{2} + \frac{1}{8} R_{\alpha \beta \delta \eta} \gamma^{\mu} \gamma^{\nu} \gamma^{\delta} \gamma^{\eta}) \psi,
\] (20c)

where the following identity was used [32] :
\[
(\nabla_{\alpha} \nabla_{\beta} - \nabla_{\beta} \nabla_{\alpha}) \psi = \frac{1}{8} R_{\alpha \beta \delta \eta} \gamma^{\delta} \gamma^{\eta} \psi
\] (24)
along with the Clifford algebra anticommutator identity \( \gamma^{\mu} \gamma^{\nu} + \gamma^{\nu} \gamma^{\mu} = 2 g^{\mu \nu} \).

Here \( R_{\alpha \beta \delta \eta} \) is the Riemannian curvature tensor.

The above equation can be rearranged further[33] yielding the equivalent final result:
\[
\left(g^{\mu \nu} \nabla_{\mu} \nabla_{\nu} + m^{2} + \frac{R}{4}\right) \psi = 0.
\] (20d)

Here \( R \) is the scalar curvature. As it is demonstrated in[3], [34] the mass term \( m^{2} \) is not essential and can be eliminated by the appropriate substitutions. In the case of fish-eye potential this is discussed also in Appendix B. In[3], sections 3 and 5, it is demonstrated 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 [33, 35], another example is given in Eq.(25) below. Additional information is presented in the Appendix E.2.

These type 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. (B.4), (with \( \gamma = 1/2 \)), e.g. read the Appendix B. That such chosen scalar curvature coincides with the curvature of the Bertrand space was demonstrated in [3] and, independently, in [36]. The obtained result, Eq.(20d), is incomplete though. To make it complete, following Schrödinger [30] 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 \( \nabla_{A\mu} = \partial_{\mu} + \Gamma_{\mu} - i e A_{\mu} \), where \( A_{\mu} \) is some kind of a vector (e.g. electromagnetic).
potential. With such a replacement, Eq.(20d) is replaced now by

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

This is the final result obtained by Schrödinger. In the mathematical literature the same equation also known as Lichnerowicz-Weitzenbock equation (more on this is presented in the Appendix E.2). Most of calculations in S-W theory involve uses of this equation [37]. The signs of \(i\) and \(e\) factors in Eq.(25) can be correctly restored. For this we have to put \(\Gamma_\mu = 0\) in the covariant derivative \(\nabla_\mu\) and then, to consult the book on quantum electrodynamics, e.g., see [38], page 66, Eq.(2.73).

Eqs.(16) and (17) now can be related to Eqs.(20d) and (25). Specifically, by putting the fine structure constant \(\alpha\) in the Lippmann-Johnson operator to zero we are arriving at Eq.(20d). For the nonzero \(\alpha\) we have to use Eq.(25) instead. Important details are presented below. This kind of logic, common in physics literature [38], does not take into account finer details, e.g. the topological considerations, etc. In the next subsection we initiate the discussion of this topic.

4.2. The topological transition between the Madelung-regular and Madelung-exceptional atoms. Motivation

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

1. 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 \(V_{eff}(r)\) is represented by \(\frac{R}{4}\). By identifying Eqs. (4) and (21d) we must identify \(\frac{R}{4}\) with \(V(r)\), Eq.(B.4), in which \(\gamma = 1/2\).

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

3. The relativistic Eq.(17) and nonrelativistic Eq.(16) look almost the same. Thanks to the work[39], both equations can be made to look exactly the same (up to the difference in the meaning of constants in these equations). This is demonstrated in the Appendix A.

Because of this circumstance, all results obtained in [3] for the nonrelativistic case can now be transferred to the relativistic case unchanged.

4. It is of interest to derive the spectrum of the Dirac-Coulomb problem by using methods developed in the Appendix A via replacing the Coulomb potential with the fish-eye potential first and then, by applying the Wong and Yeh results[39]. This is done in Appendices B and C.
In the Appendix B we demonstrate the equivalence of the Coulomb and fish-eye classical and quantum problems while in the Appendix C we demonstrate how the hydrogen atom spectrum (both non and relativistic) can be obtained using the fish-eye potential. The treatment of multi-electron atoms with help of the deformed fish-eye potential, Eq.(B.4), then follows the same steps as outlined in the Appendix C. Additional details are given in Ref.[3].

With such a background, following[38], page 75, we can now write down the fine structure $\alpha$ expansion for the spectrum of hydrogen atom ($\hbar = 1$)

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

(26)

Here $\tilde{n} = n_r + l + 1$ in accord with results of Appendix C, $j = \frac{1}{2}, \frac{3}{2}, ..., \tilde{n} - \frac{1}{2}$.

The $\alpha^4$ relativistic correction is in fact coming directly from the spin orbital interaction [38], pages 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.(B.4) ( $\gamma = 1/2$), and, by repeating calculations described in the Appendices B and C using such deformed potential, the limit $\alpha = 0$ is obtained. To achieve it requires replacing $\tilde{n}$ by $\tilde{n} + l$ in Eq.(C.3), thus resulting in the regular Madelung rule ($\hbar = 1$):

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

For $\alpha \neq 0$ a simple minded use of the expansion, Eq.(26), in Eq.(27) leads to the entirely wrong results. The relativistic effects cannot be neglected already for the hydrogen atom as is well known. They are responsible for the fine structure spectrum. Simple minded application of the same logic to the multielectron atoms then leads us to the conclusion that, based on methods utilized thus far, treatment of the Madelung-exceptional atoms cannot acquire special status. Either all atoms should obey the standard Madelung rule or they all should be exceptional.

The resolution of this paradoxical situation is obtained by providing ramifications to the item 2 (see above). That is now we 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, e.g. read [35],pages 152-154, or[33], pages 40-41, imply that Eq.(21d) makes sense only for spin manifolds. That is the quantum mechanical description of atoms exhibiting the canonical Madelung-regular behavior should be described exclusively using Eq.(20d). The account of the relativistic fine structure effects is made with help of Eq.(25). This equation is living on the spin$^c$-type manifolds[33, 35, 40]. The description of the transition- from atoms obeying the regular 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$^c$ are topologically different manifolds. 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 appendices culminating in Appendix E.4. The differences between these manifolds is in the differences in underlying spin symmetry. The topology and symmetry are intertwined as is well known. More specifically, the results depend upon whether the underlying manifold M is being orientable or nonorientable.

Topologically, this is described in terms of the 1st Stiefel-Whitney class $w_1(M)$. For the orientable manifold $w_1(M)=0$. If, in addition, the manifold can carry the spin structure (Appendix D), the second Stiefel-Whitney class $w_2(M)$ also should be zero. This is beautifully explained in Nakahara’s book[41], pages 404, 405.

The manifold M which carry spin$^c$ is described in terms of the requirement[42], page 123, $c_1(M)=w_2(M)$ mod 2. Here $c_1(M)$ is the 1st Chern class. For the spin manifolds $w_2(M)=0$ and this relation breaks down. This explains why the spin and spin$^c$ are topologically different manifolds. However, such an explanation is not describing the underlying physics well. The underlying physics is explained in Appendices E and F.

Locally, in the language familiar to physicists, it is sufficient to look at the the difference between, say, the set of compass arrows (dipoles), emphasizing the orientability of 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 suppose to illustrate. It is instructive to check if such simplified physical description can be used for visualization of spin and spin$^c$ structures. In Appendix F we are checking if such very simplified description of the spin and spin$^c$ structures, when applied to the Madelung-exceptional atoms, makes sense. Such simplified treatment should be considered only as qualitative/nonrigorous. The rigorous treatment is 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 are coming (in part) from the spin-orbital interactions. Ramifications of such demonstration will link the Hund rule, the LS, JJ and LSJ couplings schemes to the \( \text{spin} \rightleftharpoons \text{spin}^c \) topological transition.

Following [38], page 74, without loss of generality we have (for the centrally symmetric Coulombic field):

$$\frac{i}{2}\sigma^{ab}F_{ab} = \pm ie\sigma \cdot E = \pm iZ\alpha \sigma \cdot \vec{r} / r^2,$$

where $\vec{r}$ is the unit vector. A quick look at Eqs.(17),(18) allows us to realize that just obtained result enters into the Lippman-Johnson operator, Eq.(18). Thus, at least for
the case of single electron, Eq.s (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 \( \alpha \), the spin-orbit coupling interaction term[38],pages 69-75. This means that Eq.(17) contains information on spin-orbit coupling to all orders in \( \alpha \) 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 presented in the series of three papers by Blume and Watson[46, 47]. These papers and references therein indicate that, very fortunately, the complicated expressions can be squeezed back to the spin-orbital interaction Hamiltonian known for the hydrogen atom with the appropriately redefined coupling constant to be determined experimentally. This fact is not affecting the analytical structure of Eq.(17) and, therefore, the exact mapping- from the relativistic to nonrelativistic case-described in the Appendix A remains intact. Since the spin-orbit interaction Hamiltonian is the first order in \( \alpha \) result, it surely cannot compete with the topological arguments [35], pages 152-154, or [33], pages 40-41, valid to all orders in \( \alpha \). Just presented 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 for explanation of the normal to superconducting topological transition at the atomic level

Already in subsection 1.1. we noticed that the diamagnetic properties of hydrogen atom are making it superconductor at the atomic level. None of other hydrogen -like atoms , e.g. Li,Na,K, Rb,Cs are diamagnetic. In fact, they are all paramagnetic. At the same time, not at all surprising, all noble gases are diamagnetic. The hypothesis by Ashcroft and Ginzburg about hydrogen superconductivity brings along the following questions. 1. If the atomic hydrogen is a superconductor (since it is subject to the Meissner effect), can we call the noble gases as superconductors? 2.If condensed and solidified, will all these elements become superconducting? 3. Under the appropriate pressure-temperature conditions, will all these elements become at least conductors? 4. Are there properties, other than zero resistivity, indicating that a given solid is superconductor? Some answers to questions 1-3 can be found in [5]. As for question 4, we would like to mention the following. Historically, the Madelung-exceptional palladium is the first element allowing us to find an answer to the question 4. In subsection 1.2. it is stated that Pd is not superconductor but PdH\(_x\) is. Here, as in section 1.2., we are talking first about PdH\(_x\) under ambient pressure. Negligibly small amounts of the absorbed hydrogen make palladium superconducting and its \( T_c \) is going up directly proportional to the amount of absorbed H. Since the absorption is reversible (that is, it costs zero energy) palladium is fantastic catalyst and hydrogen storage provider[11]. The property of reversible absorption allows to apply to solid palladium the method of quasiaverages developed by Bogoliubov [13],[14]. Although eventually this method was applied to many order-disorder phase transitions,
initially it was applied to the BCS superconductors. Method of quasiaverages explains why the superconducting condensate is not number-conserving. That is, the number of Cooper pairs in superconducting condensate is not conserved. Below we argue that:
a) all Madelung-exceptional atoms are superconductors in the sense of conventional mathematical description of superconductivity done either within a framework of the Ginzburg-Landau or, more sophisticated, Seiberg-Witten theory; 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 reconsider the equivalence between Eq.s(17) and (25) first. Thus far we used plausible arguments following book by Itzykson and Zuber [38], page 74. These plausible arguments can be made rigorous using results of 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 books by Jost [35] and Naber [40]. To expedite matters we also recommend reading, at least the first couple pages, of the review by Donaldson [38].

To make our first step, that is to restore Eq.(28) using the S-W equations, we shall follow the paper by Naber [40,49]. Using this paper it is sufficient to consider these equations in the flat Minkowski spacetime $\mathbb{R}^{1,3}$. In such a case the covariant derivative $\nabla_A \mu = \partial_\mu + \Gamma_\mu - ieA_\mu$ should have $\Gamma_\mu = 0$. For complacency with [40,49] we rewrite $\nabla_\mu$ as $\nabla_\mu = \partial_\mu + A_\mu$. Then, the first of S-W equations can be written as

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

To write the second of S-W equations, it is essential to keep in mind the origin of these equations. At first look, it appears that it is sufficient to consult the book of Jost [35] or, the paper by Witten [50]. From both sources it follows that the S-W equations emerge as generalization of the G-L equations of superconductivity. Thus, the solutions of S-W equations must contain vortices/monopoles-typical solutions of G-L equations. At the very advanced level, this fact was reconfirmed by Taubes [51]. In the present case our Eq.(25), although included into the S-W formalism, requires some additional explanations. These are presented in the Appendix E, thus making our atomic physics problem an intrinsic part of the S-W formalism.

At the same time, the treatment of G-L equations begins typically with writing of the G-L functional whose variation is producing the set of G-L equations. The self-duality considerations allow then to simplify calculations considerably and to reduce the order of these equations-from 2 to 1. Very detailed exposition of this topic is given in our book [52], chapters 5.6. Such a reduction was performed first in the context of the Yang-Mills fields by Bogomolny whose methodology was extended to S-W theory, where the 1st order self-dual equations are also used. Naber’s paper [49] also uses this reduction. Thus obtained S-W solution, even though reproduces the result, Eq.(28), is not $L^2$ normalizable. Similar cases of $L^2$ normalizable solutions are discussed in [53]. For the S-W monopoles on Kähler and symplectic manifolds more advanced treatment is presented in [54]. These lecture notes use essentially
the results of Taubes[51].

With these remarks we return back to Eq.(25) without mass term. It can be eliminated as it was explained in[3,34]. Let $D_A = \gamma^\mu \nabla_{A\mu}$ then, using the massless Eq.(25), we obtain:

$$\int_M (D^+_A \bar{\psi}, D_A \psi) \, dvol = \int_M \{(\nabla^+_A \bar{\psi}, \nabla_A \psi)^2 + \frac{R}{4} (\bar{\psi}, \psi) + \frac{1}{2} (F^+(A) \bar{\psi}, \psi)\} \, dvol = 0,$$  \hspace{1cm} (30)

where we used the Hermitian scalar product $(\cdot, \cdot)$, and the self-dual portion of the $F(A)$, that is $F(A)^+ = \frac{1}{4} (F(A) + *F(A))$. The notion of spinor bundle (Appendix D) allowed us to write $F(A) \psi = F(A)^+ \psi$, e.g. read page 76 of Ref.[55].

The result, Eq.(30), should be compared against the standard G-L functional:

$$S_{G-L}(A, \psi) = \int_M \{(\nabla_A \psi)^2 + |F(A)^+|^2 + \frac{R}{4} |\psi|^2 + \frac{1}{8} |\psi|^4 \} \, dvol.$$  \hspace{1cm} (31)

To make Eqs.s(30) and (31) to coincide formally, following Jost[35], we need:

- a) to write the 2-form $F(A)^+$ as $F(A)^+ = F(A)^+_{ij} \gamma^i \gamma^j$, (b) to assume that $F(A)^+_{ij} = \frac{1}{4} (\gamma_i \cdot \gamma_j \psi, \psi)$. Here the dot $\cdot$ represents the Clifford multiplication (Appendix D). After that, we formally obtain:

$$S_{S-W}(A, \psi) = \int_M \{(D_A \psi)^2 + |F(A)^+|^2 - \frac{1}{4} (\gamma_i \cdot \gamma_j \psi, \psi) \gamma^i \gamma^j \} \, dvol = S_{G-L}(A, \psi) \hspace{1cm} (32)$$

leading to the 1st, Eq.(29), and to the 2nd

$$F(A)^+ = \frac{1}{4} (\gamma_i \cdot \gamma_j \psi, \psi) \gamma^i \gamma^j \hspace{1cm} (33)$$

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

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

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

implies

$$\frac{1}{2} \Delta |\Phi|^2 \geq (\nabla^+_A \nabla_A \Phi, \Phi). \hspace{1cm} (34b)$$

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

$$\Delta |\psi|^2 \leq - \frac{R}{2} |\psi|^2 - (F^+(A) \bar{\psi}, \psi). \hspace{1cm} (35a)$$

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

\[ \Delta |\psi|^2 \leq -\frac{R}{2} |\psi|^2 - \frac{1}{4} |\psi|^4. \]  

(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 \( \psi \) produces:

\[ \frac{1}{2} \int_M |\psi|^4 \, d\text{vol} \leq - \int_M R |\psi|^2 \, d\text{vol} \leq \int_M R^2 \, d\text{vol}. \]  

(36)

Following Jost[35] and by using Eq.s(31)-(33) we obtain finally:

\[ \int_M |F(A)^+|^2 \, d\text{vol} \leq \int_M \frac{R^2}{4} \, d\text{vol}. \]  

(37)

Up to extra factor of \( \frac{1}{4} \) in the r.h.s., this inequality coincides with the inequality, Eq.(3.5), obtained in the seminal paper by Witten[56]. In our case, the obtained inequality should be interpreted differently. The scalar curvature-the product of electron-electron interactions-controls existence or nonexistence 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 the gauge transformations. In the present case the gauge group \( \mathcal{G} \) is made of maps \( f \) - from M to \( S^1 \). Let \( u \in \mathcal{G} \), then the gauge transformations of S-W equations are described by (not to be confused with the scalar multiplication):

\[ (A, \psi) \rightarrow (A + 2u^{-1}du, u^{-1}\psi) \]  

(38)

The moduli space \( \mathcal{M} \) are formally defined as a quotient

\[ \mathcal{M} = \text{solutions}/\mathcal{G} \]  

(39)

The most relevant for us is the case when \( \mathcal{M} = 0 \). In such a case the S-W equations possess only finite number of localized solutions. This fact provides justification for the existence of finite number of Madelung anomalous solutions. It the Appendix C we outline different approach to this result.

Surprisingly, in the version of S-W theory considered by Witten[56], the case \( \mathcal{M} = 0 \) happens to be also the most interesting one. It is associated with the fact that the manifold M posses almost complex structure [33], e.g. read the Lemma on page 89. In physical language, this means that the (semi)classical limit of quantum mechanics on such manifolds are well defined because they admit
well defined classical trajectories. This conclusion was reached by Witten[56] already in his first original paper on the subject.

Mathematically, the condition $\mathcal{M} = 0$ occurs for manifold $\mathcal{M}$'s for which

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

Here $\tau[\mathcal{M}]$ is the signature and $\chi[\mathcal{M}]$ is the Euler's characteristic of $\mathcal{M}$, while $c_1(L)$ is the 1st Chern class of the line bundle $L$ (connected with $S^1$ for the $spin^c$ manifolds as explained in the Appendix D). Connection with the Atiyah-Singer index theorem can be seen directly by reading page 64 of Ref.[33]. It is associated with the vanishing of the 2nd Chern class $c_2(S^+_n \otimes L)[\mathcal{M}]$. Here $S^+_n$ is a part of the spinor bundle defined in the Appendix D. In the Appendix E 4. physically motivated explanation of $spin^c$ manifolds is given. It is associated with phenomenon of superconductivity. Such an explanation is plausible (makes sense) since the S-W theory is reducible to the G-L theory whose origins are in superconductivity [50].

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

To our knowledge, in this work for the first time the superconducting nature of the Madelung-exceptional atoms is elucidated. Historically, however, 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 [61], [66]. Obviously, for the atomic nuclei as much as for the hydrogen atom, or the Madelung-exceptional atoms, there is no point to talk about the macroscopic evidence of superconductivity. The superconductivity for these systems should be understood in terms of Bogoliubov’s quasiaverages introduced in subsection 1.2. This means that breaking of $U(1)$ gauge invariance associated with nonconservation of Cooper pairs is mathematically reflected in emergence of quasiaverages [13],[14]. At the scales of atomic nuclei the 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 in 1959 formulated the following problem [74]. 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 [75]. Since the spectroscopy is working for granular superconductors, it should be working as well 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 the superconductivity by applying the concept of quasiaverages to the reversible absorption. To do so requires the Madelung-exceptional metal to be placed into gaseous hydrogen environment.

Since nuclear excitations are, in fact, the excitations of quark-gluon plasma, the nuclear spectroscopy should seamlessly merge with the spectroscopy of hadrons and, hence, with excitations of the Yang-Mills fields. Such line of research was initiated in our works [76],[77]. 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 recently have found their place in chemistry [78].

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

\[ D^2 \psi = 0, \text{ where } D^2 = \nabla^* \nabla + K. \] (41)

Here \( D^2 \), defined in Eq.(E.12) , is the Hodge Laplacian. For the \( \text{spin} \) manifolds \( K = R^S \) implying that we are dealing with Eq.(4) while for the \( \text{spin}^c \) manifolds \( K = R^S + F^S \), e.g. see (Eq.E.16) and we are dealing with Eq.(25). As explained in the Appendix E.4., the superconductivity takes place on the \( \text{spin}^c \) manifolds only. Second, the Hodge Laplace, Eq.(41), is just the linearized analog of the respective Hodge-like Laplacian-type equation for the Yang-Mills fields [79]. Thus, the nuclear superconductivity excitations are, in fact, also excitations of the Yang-Mills fields.

Since our Ref.[77] is devoted entirely to study of the millennium Yang-Mills gap problem, it is hoped, that the present work might provide eventually its own contribution to the gap problem.

Following [76],[77] as well as [80],[81] and using Eq.(E.20), we begin with the Hamiltonian, \( \hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_V \), and replace the matrix element \( V^{(0)}_{kk'} \) by the constant \(-g\).

The resulting Hamiltonian is given then by Eq.(5.42) of [77], i.e.

\[ \hat{\mathcal{H}} = \sum_f 2\varepsilon_f \hat{N}_f - g \sum_f \sum_{f'} \hat{b}_f^\dagger \hat{b}_{f'}, \] (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 \( c_f^+ \), \( \sigma \) are obeying 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 [80] : \( \hat{\nu}_f = c_f^+ + c_f^+ - c_f^+ - c_f^- \). It is taking care of the number of unpaired fermions at each level \( f \). By construction, \( [\hat{\mathcal{H}}, \hat{N}_f] = [\hat{\mathcal{H}}, \hat{\nu}_f] = 0 \). These commutators permit us to make a subdivision \( \hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 \) and to count configurations beginning with the situation when \( g = 0 \) since the eigenvalues \( \nu_f \) of the seniority operator \( \hat{\nu}_f \) remain unaffected by \( g \). In such a case let \( \hat{\mathcal{H}}_1 \) describe the states without Cooper pairs, that is it describes the Hilbert space sector for which \( \nu_f = \sigma \). Accordingly, \( \hat{\mathcal{H}}_2 \) is to be associated with the sector for which \( \nu_f = 0 \). Such a
subdivision produces a remarkable and unexpected result: the matrix elements of $\hat{H}_2$ are calculated with help of the **bosonic-type** commutation relations. These are
\[
[\hat{b}_f, \hat{N}_{f'}] = \delta_{ff'} b_f \quad \text{and} \quad [\hat{b}_f, \hat{b}_f^+] = \delta_{ff'} (1 - 2\hat{N}_{f'})
\] (43)

Even though these are bosonic commutators, but 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 [80], but more elegantly in [81]. The problem was reduced to finding the spectrum of the Richardson-Gaudin one dimensional spin chain. Its excitation spectrum resemble that for the nonideal Bose gas.

Before writing down this spectrum of $H$, we define $\Omega_n$ as the pair degeneracy of the level $n$, that is $\Omega_n$ is the number of values of $f$ for which $\varepsilon_f = \varepsilon_n$. Omitting all the details given in [76],[77],[80],[81], we introduce the function $F(E)$ via
\[
F(E) = \sum_n \Omega_n (2\varepsilon_n - E)^{-1}
\] (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 by Cooper [82]. It paved a way for 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 pairs wave functions so that the total energy of $N$ pairs is the sum of the respective energies of $N$ Cooper pairs. This assumption allows us to write the spectrum as
\[
F(E_{p_i}) = g_i^{-1}, \quad g_i = g[1 + 2g \sum_{j \neq i} (E_{p_j} - E_{p_i})^{-1}]^{-1}; \quad i = 1, ..., N.
\] (45)

Presented results serve only to introduce our readers to more complicated problems such as a) crossover: from the atomic limit to the bulk metal and, b) effects of finite temperatures. The crossover problem (even including the temperature effects) was discussed in detail in section 5 of [75]. Since this review was published in 2001, we decided to provide up to date (2020-2021) results. In [83] the results of Richardson and Sherman [80] were elaborated further. In [84] and [85] the results of [75] were significantly elaborated. In [86] the results on nanoclusters of high temperature superconductors were reported.

### 7. Summary and discussion

Study of the high temperature in superconductors [5] cannot progress without discoveries of new guiding principles. The purpose of this paper is to supply several new guiding principles. These are based on theoretical explanations of several empirical observations. These are: a) the majority of Madelung-exceptional elements yield the highest $T'_c$'s to
date, b) the Madelung exceptionality is linked with the property of reversible hydrogen absorption yielding exceptionally high concentration hydrides of these elements [10] [11], [87], pages79-84. Among all these Madelung-exceptional elements. The Madelung-exceptional elements were in use till now without emphasis on their Madelung exceptionality. Empirically, this exceptionality was noticed due to the unusual property-the 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. From this angle it is not too surprising that it was Pd which was used initially in the cold fusion experiments https://en.wikipedia.org/wiki/Cold_fusion.

The empirical ability to absorb large amount of hydrogen singled out Madelung-exceptional metals as likely candidates of high $T_c$ superconductors. The fact that the hydrogen absorption is reversible (under the appropriate experimental conditions [88]) caused us to use Bogoliubov’s method of quasiaverages [13],[14] associated, in the present case with Cooper pairs nonconservation. This property is characteristic of superconductivity. As we argued in section 6, the phenomenon of superconductivity exist on many scales [89]. When looking at the Madelung-exceptional elements one should not anticipate all of them to be superconductors in traditional sense without hydrogen environment. But once such environment is provided (under appropriate pressure-temperature conditions) they all are becoming superconductors in traditional sense. This is indeed the case, for example, for Pd. Pd is not a superconductor but in the presence of small amount of gaseous hydrogen it becomes superconducting under usual ambient conditions (e.g. read the subsection 1.2.). Since the superconductivity is observed at scales ranging from atomic nuclei to the scales of neutron stars [89], it is only natural to search for superconductivity at the atomic scales. It was done in this paper. Here it is demonstrated analytically (by non trivially solving the quantum many-body problem and invoking some results from S-W theory) that only the Madelung-exceptional atoms possess the superconducting property. It 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 obtained results to the atomic clusters by relying on methods developed for the superconducting clusters. Since the size of clusters is an adjustable parameter in these calculations, the problem of crossover- from the atomic scales to scales of bulk metals- was briefly outlined as well. In this regard, Ref.[90], might serve as an excellent point of departure for further studies.

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APPENDIX A. Mapping the Dirac equation into Schrödinger-like
Following Wong and Yeh [39], we shall employ the system of units in which \( c = 1, \ h = 1 \). Then, taking into account that in discussing Eq.s(16) and (17) we introduced the factor \( K \) in the nonrelativistic case and \( \Gamma \) in the relativistic, we argued that the combination \( K (K + 1) = l (\kappa) (l (\kappa) + 1) = l (l + 1) \) in the nonrelativistic case and \( \Gamma (\Gamma + 1) = \gamma (\kappa) (\gamma (\kappa) + 1) \) in the relativistic. Therefore Eq.(17) acquires the form

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

The nonrelativistic \( l \) is replaced now by the relativistic \( \kappa = \pm (j + \frac{1}{2}) \) and \( \gamma \kappa = \pm [\kappa - (Ze^2)^2] \), see Eq.(19). In the case of discrete spectrum \( m^2 - E^2 > 0 \).

Therefore, it is convenient to introduce the new variables as follows:

\[
\mu = \left[ m^2 - E^2 \right]^{\frac{1}{2}}, \rho = 2\mu r, \omega = 4Ze^2E/\mu. \]

In terms of these variables Eq.(A.1) acquires standard form of the radial equation for hydrogen atom

\[
\left[ \frac{1}{\rho^2} \frac{d}{d\rho} \rho^2 \frac{d}{d\rho} - \frac{l (\kappa) (l (\kappa) + 1)}{\rho^2} + \omega - \frac{1}{4}\beta_n R_{N,l(\kappa)}(\rho) = 0 \right. \tag{A.2}
\]

\[e.g. \, see, \,[48], \, Eq.(16.7). \]

This transformation allows us to apply unchanged

the same methodology as was developed in [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 1st paper on quantum mechanics the standard Schrödinger equation

\[
\left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \varphi = \frac{2m}{\hbar^2} (E - V) \varphi \tag{B.1}
\]

is obtainable variationally from the Hamilton-Jacobi equation[34]

\[
\psi_x^2 + \psi_y^2 + \psi_z^2 = 2m(E - V), \tag{B.2}
\]

where \( \psi = \hbar \ln \varphi \). Next, following Luneburg[22] we use the canonical change of variables:

\( \xi = x\xi, \eta = y\eta, \zeta = z\zeta; x = \omega x, y = \omega y, z = \omega z \) subject to the condition

\[\psi + \omega = x\xi + y\eta + z\zeta \]

in Eq.(B.2). When \( V \) is the attractive Coulombic potential and such transformations are applied to Eq.(B.2) the result is

\[
\frac{1}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \varphi + \beta_n \left( \frac{1}{1 + x^2 + y^2 + z^2} \right)^2 \varphi = 0, \tag{B.3}
\]
where $\beta_n = \left( \frac{Ze}{E_n} \right)^2$. Just described chain of transformations is converting the eigenvalue problem, for Eq.(B.1), into the Sturmian problem, for Eq.(B.3). The Coulombic potential $V_C = \frac{\text{const}}{r}$ in Eq.(B.1) is converted into the Maxwell’s fish-eye potential $V_F = \frac{\text{const}}{1+(r/a)^2}$, $r^2 = x^2 + y^2 + z^2$. Here $a$ is a constant In Eq.(B.3) we select $a = 1$.

The conversion into the Sturmian problem is having an additional advantage. It is converting Eq.(3) into conformally invariant Eq.(4) [3]. Uses 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 account of the spin-spin interactions). These are accommodated into the formalism with help of the results of section 4 and Appendix E. Applications of conformal transformations to Eq.(B.3) converts Maxwell’s fish-eye potential $V_F$ into its conformally deformed form:

$$V(r) \equiv V(x, y, z) = -\left( \frac{a}{r} \right)^2 \left[ \frac{n_0}{(r/a)^{\gamma} + (r/a)^{\gamma}} \right]^2.$$  \hspace{1cm} (B.4)

This results in replacement: $V_{eff} = V_F$ in Eq.(4) by the $V(r)$, Eq.(B.4). Details are given in [3]. Application of scaling analysis-the simplest of conformal transformations-indicates that only two exponents $\gamma$ are permissible. Using $\gamma = 1$ recreates back the Coulombic fish-eye potential for the hydrogen atom. Using $\gamma = 1/2$ recreates the multielectron effects for any multielectron atom. Furthermore, using Eq.(B.4) with $\gamma = 1/2$ numerically produces exactly the same results as those known for the Hatree-Fock potential. The value of the constant $\beta_n$ is not affected by uses of conformal transformations. The additional bonus of using $V(r)$, Eq.(B.4), is coming from the very nontrivial exact conversion of the $V(r)$ into potential obtained by Perlick [23] in his studies of the generalized Bertrand theorem.

**APPENDIX C. Calculation of the hydrogen and the Madelung-regular atomic spectra.** Alternative explanation of the discretness of moduli space

a) **Calculation of the spectrum.** To treat the accidental degeneracy in the spectrum of hydrogen atom Fock developed entirely new method of solving the spectral problem for hydrogen atom[34] by considering the solution of this problem on $S^3$. Since Eq.(B 3) 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.(B 3) in $\mathbf{R}^3$ by the treatment on $S^3$ in accord with the results of subsection 3.3. By lifting Eq.(B3) to $S^3$ it is converted to Eq.(11a). In Eq.(11a) we have to present $Y_{nlm}(\alpha, \theta, \phi)$ as $\Psi_{nl}(\alpha)Y_{lm}(\theta, \varphi)$ so that Eq.(11a) acquires the form:

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

29
Here \( I_{nl} = \frac{-(Ze)^2}{2|E_{nl}|} \) in the nonrelativistic case. In the relativistic case we have to make a replacement \( l \rightarrow l(\kappa) \) and to write \( I_{nl} = \left( \frac{\omega}{4} \right)^2 \).

All details are given in the Appendix A and must be performed with account that \( E \) is describing bound states. Next, we write \( x = \cos \alpha \) and, by rewriting \( \Psi_{nl}(\alpha) \) in terms of such variable and representing it in the form \( \Psi_{nl}(\alpha) = (1 - x^2)^{\frac{n}{2}}F_{nl}(x) \), Eq.(C1) is converted into equation

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

Eq.(C2) is the equation for the Gegenbauer polynomials. Using this fact we obtain, after some calculation: \( I_{nl} = (n + l + 1)^2 - 1 = \tilde{n}^2 - 1 \).

Let now \( \tilde{n} = 2F + 1 \). Then, \( \tilde{n}^2 - 1 = 4F(F + 1) \). Using this information, consider, instead of Eq.(11a) (that is Eq.(C.1)) the equation \( \mathcal{L}^2Y_{nlm} = (I_{nl} - E)Y_{nlm} \) in which \( E \) is the fixed parameter. The necessity of doing this is explained in the section 4 and Appendix F of [3]. 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

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

Here \( n = n_r \) in the standard quantum mechanical notations. For the Dirac case we obtain as well:

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

where \( \omega \) is defined in the Appendix A. The result, Eq.(C.4), coincides with Eq.(3.26) of Ref.[39]. By restoring back \( c, \hbar \) and, hence, the \( \alpha \), and using Eq.(C 4) we reobtain back the known Dirac spectrum.

The Madelung-regular spectrum emerges as solution of Eq.(11b). In view of the fact that Eq.(11b) emerges as modification of Eq.(11a) caused by change: from \( \gamma = 1 \) to \( \gamma = 1/2 \) in Eq.(B.4). Eq.(C.1) changes accordingly also. This leads to some changes in Eq.(C.2) while keeping \( I_{nl} = \frac{-(Ze)^2}{2|E_{nl}|} \) unchanged. Due to changes in Eq.(C.2), the spectrum, that is the Eq.(C.3), also changes resulting in Eq.(27) of the main text. Details are given in [3].

b) Discretness of the moduli space. As it follows from results of section 5, we need to provide an evidence that, upon relativization, not all atoms become the Madelung-exceptional. We would like to achieve this by using the inequality Eq.(36). In this inequality we shall choose \( M = S^3 \). On \( S^3 \) we shall use properly normalized spherical
eigenfunctions $Y_{n+l,m}(\alpha, \theta, \varphi)$ defined in Eq.(11b), see also [18]. Account of relativistic effects leads to the replacement of quantum number $l$ by the $l(\gamma \kappa)$, defined in Eq.(A.1). Also, instead of $I_{nl} = -\frac{2(n_{r}^2)}{|E_n|} = \tilde{n}^2$, in view of Eq.(C.3), 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.(C.4). Since the area of $S^3$ is known constant, the inequality, Eq.(3.6), 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 the integer nonnegative $Z$’s. It is clear then, that there could be only a countable number of $Z$’s or no $Z$’s 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 resulting from Eq.(36) equality will not contain the parameter $Z$ at all and, therefore, neither the inequality, Eq.(36), nor the equality originated from Eq.(36), make no physical and, even mathematical, sense when $Z$ is absent. That is relativistic effects are completely ignored.

APPENDIX D. Spin structures. Group-theoretical and topological aspects

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

D.1. Vector and spinor representations of Clifford algebras

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

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

where $T(V)$ is the tensor algebra and $I(V, g)$ is the ideal created by $x \otimes x + g(x, x)1, \forall x \in V$. If we define a map $x \rightarrow c(x)$ such that $x \otimes x + g(x, x)1 \rightarrow c(x) \otimes c(x) + g(c(x), c(x))1$, then, there is a unique algebra homeomorphism: $Cl(V, g(x)) \rightarrow Cl(c(V), g(c(x)))$. In such a way in section 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 possible as well. Let now $(e_1, ..., e_n)$ be a $g$-orthonormal basis of $V$, then

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

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 $\Lambda^*V \rightarrow Cl(V, g)$, that is

$$e_{i_1} \wedge \cdots \wedge e_{i_k} \rightarrow e_{i_1} \cdots e_{i_k}$$

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This fact is compatible with the observation that the ideal \( I(V, g = 0) \) in Eq.(D.1) converts the Clifford algebra into the Grassmann algebra. Thus, the Clifford algebra is the deformation of the Grassmann algebra. The canonical isomorphism, Eq.(D.3), 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 the Appendix E below.

The above isomorphism does not depend upon 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) and \( = -1 \) (if \( k \) is odd). Using these definitions we are in the 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

\[
Pin(V) : \{a = e_1 \cdots e_k \mid g(e_i, e_i) = 1, \forall i = 1 \div k\}, \tag{D.4a}
\]

while

\[
Spin(V) : \{a = e_1 \cdots e_{2k} \mid g(e_i, e_i) = 1, \forall i = 1 \div 2k\}. \tag{D.4b}
\]

By design, for \( Spin(V) aa^t = 1 \). Let \( \rho(a)v = ava^t, v \in V \), then one can construct a surjective homeomorphism \( \rho(Pin(V)) \rightarrow O(V) \) while use of \( Spin(V) \) results in \( \rho(Spin(V)) \rightarrow SO(V) \). 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 \( \rho(a)v = v, \forall v \in V \).

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 obtained result allows us to make further step by defining the \( Spin^c(V) \) group. To do so, requires some preparations.

**First**, we have to define the complexified Clifford algebra \( Cl^C(V) = Cl(V, g) \otimes \mathbb{C} \).

**Second**, we have to define the chirality operator \( \Gamma \) via

\[
\Gamma = i^m e_1 \cdots e_n \in Cl^C(V) \tag{D.5}
\]

so that \( m = n/2 \) for \( n \) even and \( m = (n + 1)/2 \) for \( n \) odd. Evidently, \( \Gamma^2 = 1, \Gamma v = v \Gamma \) for even \( n \) and \( \Gamma v = -v \Gamma \) for odd \( n \). That is \( \Gamma \) is operator of involution. This induces a decomposition of \( Cl^C(V) \) into \( Cl^C(V)^\pm \) parts. The decomposition is a bit involved.

**Third**, in \( V \otimes \mathbb{C} \) space we must:

\( a) \) introduce a subspace \( W \) made of vectors

\[
\eta_j = \frac{1}{\sqrt{2}} (e_{2j-1} - e_{2j}), \quad j = 1, \ldots m, \tag{D.6}
\]

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

\[
< \eta_i, \eta_j > \mathbb{C} = 0 \quad \forall j. \tag{D.7}
\]

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

\[
\bar{\eta}_j = \frac{1}{\sqrt{2}} (e_{2j-1} + e_{2j}), j = 1, \ldots m, \tag{D.8}
\]
so that, instead of Eq.(D.7), we obtain:

\[ <\eta_j, \bar{\eta}_j> \equiv \|\eta_j\| \quad \forall j. \quad (D.9) \]

Clearly, Eq.(D.9) has a quantum mechanical meaning to be amplified below.

**Definition D.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, \( \forall s \in S_n = \wedge W \) the endomorphism \( \text{End}_C(S_n) \) denoted as \( \rho(w) \) is defined as

\[
\rho(w)s : = \sqrt{2}\varepsilon(w)s, \quad (D.10a) \\
\rho(\bar{w})s : = -\sqrt{2}i(\bar{w})s. \quad (D.10b)
\]

Here \( s = \eta_{j_1} \wedge \cdots \wedge \eta_{j_k}; 1 \leq j_1 < \cdots < j_k \leq m; \varepsilon(\eta_j) = \eta_j \wedge \eta_{j_1} \wedge \cdots \wedge \eta_{j_k}; \)

\[
i(\bar{\eta}_j)s := \begin{cases} 0 & \text{if } j \neq \{j_1, \ldots, j_k\} \\
(-1)^{l-1}\bar{\eta}_j \wedge \cdots \wedge (\bar{\eta}_j)^0 \wedge \cdots \wedge \eta_{j_k} & \text{if } j = j_l \end{cases} \quad (D.11)
\]

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

\[ S_n = S_n^+ \oplus S_n^- \quad (D.12) \]

Here \( S_n^+ \) and \( S_n^- \) are eigenfunctions (half spinors) of the operator \( \Gamma \) whose eigenvalues are \( \pm 1 \).

**Definition D.2.** The representation \( \rho \) of \( \text{Spin}(V) \) given by Eq.s(D.10a) and (D.10b) on the spinor space \( S_n \) is called spinor representation. The same, but on \( S_n^+ \) and \( S_n^- \) is called half spinor representation.

Spinor representation is an unitary presentation \cite{33}. It preserves the Hermitian product. Therefore it is ideally suitable for the quantum mechanical calculations.

To extend these results for odd \( n \), it is helpful to know \cite{35} that : a) for \( \text{dim } V = 2n \), \( \text{Cl}^e(V) \simeq \mathbb{C}^{2^n \times 2^n} \), b) for \( \text{dim } V = 2n + 1 \), \( \text{Cl}^e(V) \simeq \mathbb{C}^{2^n \times 2^n} \oplus \mathbb{C}^{2^n \times 2^n} \).

With this information, the odd dimensional space \( V \) does not create additional problems. The spinor and half spinor representations admit unique extension to \( \text{Spin}^e(V) \).

**Definition D.3.** A group \( \text{Spin}^e(V) \) is a subgroup of multiplicative group of units (that is of elements having an inverse) of \( \text{Cl}^e(V) \). It is generated as a surjective mapping: \( \text{Spin}(V) \times S^1 \rightarrow \text{Spin}^e(V) \), where \( S^1 \) is the unit circle in \( \mathbb{C} \). If \( a \in \text{Spin}(V) \) and \( z \in S^1 \) then, the kernel of this mapping is \( az = 1 \) is implying: \( a = z^{-1} \in \text{Spin}(V) \cap S^1 \).
Definition D.4. \( \text{Spin}^c(V) \) is isomorphic to \( \text{Spin}(V) \times \mathbb{Z}_2 S^1 \), where the \( \mathbb{Z}_2 \) action identifies \((a, z)\) with \((-a, -z)\). \( \text{Spin}^c(V) \) yields a nontrivial double covering \( \text{Spin}^c(V) \rightarrow SO(V) \times S^1 \).

The physical meaning of \( \text{Spin}^c(V) \) was never discussed in mathematical literature. It is explained below, in the subsection E. 4.

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 Clifford bundle (see below). In general relativity such a bundle is known as frame bundle[31]. Uses of vierbeins \( e_a^\mu(x) \) in subsection 4.1. reflect just this fact. The spinorial analysis elevates this concept one level above just described. Specifically, it begins with the following

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

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

Since the fiber \( \text{Spin}(n) \) operates on the spinor space \( S_n \), Eq.(D.12), 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 D.7. The Spinor bundle \( \mathfrak{S}_n \) is defined as
\[
\mathfrak{S}_n = \tilde{P} \times_{\text{Spin}(n)} S_n
\] (D.13)

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

Definition D.6. Bundles \( Cl(P) \) and \( Cl^C(P) \) defined below
\[
Cl(P) = P \times_{SO(n)} Cl(V),
\] (D.14a)
\[
Cl^C(P) = P \times_{SO(n)} Cl^C(V)
\] (D.14b)

are called Clifford bundles.

From the definition of Clifford bundles it follows that the creation of such bundles do not require spin or spin\(^c\) structures. However, they can exist on such structures as well. This will be further studied in the next appendix in the context of Dirac operators.
The fundamental issue is: *If there a connection between the Clifford and Spinor bundles, what physics such a connection describes?* To answer this question requires introduction of many nontrivial facts to be described below.

**APPENDIX E. Dirac operators on Clifford and spinor bundles**

The purpose of this appendix is to demonstrate that the Eq.(25) obtained by Schrödinger accounts for all quantum many-body effects for the atomic multielectron system. At the present, the relativistic many-body effects are treated with help of the relativistically extended Hartree-Fock variational methods [24]. In the nonrelativistic limit the Hartree-Fock calculations end up with the eigenvalue Eq.(3). It does not obey the superposition principle though. This happens to be a fundamental problem for development quantum mechanics of many-body systems as explained in detail in the book by Tomonaga[57]. He calls the equations like Eq.(3) De Broglie-type. He argues that the formalism of second quantization, essential for development of quantum field theory, is applicable only to the Schrödinger-type equations for which the superposition principle holds. This is also explained in another of his books[58], page108. Ignoring the supersposition principle makes the underlying equations formally purely classical. That is in such equations the Plank constant \( \hbar \) can be eliminated by the appropriate changes of variables and rescaling. This paradoxical situation is explained in detail in our work[34]. To our knowledge, in physics literature the second quantization method is used in many-fermion theory with or without account of the superposition principle [59]. In this work, we strictly follow the philosophy of Tomonaga since it is in formal accord with the Hodge-de Rham theory whose basics we describe below.

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

**E.1. Clifford algebra versus second quantization**

A quick and very informative introduction to the formalism of second quantization is given in books by Tomonaga [58,59]. From them, it follows that such a formalism was initially designed to treat the processes involving interaction of light with matter. Since photons (bosons) are relativistic objects, this requires fermions to be treated relativistically as well. That is with help of the Dirac equation. However, many books on the second quantization begin with the canonical anticommutation relations given by

\[
\{a_i, a_j^+\} = \delta_{ij}, \quad \{a_i, a_j\} = 0, \quad \{a_i^+, a_j^+\} = 0.
\] (E.1a)

From these relations the relativistic aspects of the second quantization of fermions are not apparent at all! However, following Rosenberg [60], 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.s(E.1a) we obtain at once
\[
\{ \hat{e}_i, \hat{e}_j \} = -\{ \hat{e}_i^+, \hat{e}_j^+ \} = -2\delta_{ij}, \{ \hat{e}_i, \hat{e}_j^+ \} = 0. \tag{E.2}
\]
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
\[
d = \sum_i a_i^+ \nabla_i \text{ and, } d^+ = -\sum_i a_i \nabla_i \equiv \delta^{[4]}. \tag{E.3}
\]
E.2. Assortment of the Weitzenbock-Lichnerowicz formulas: Hartree-Fock versus Hodge-de Rham

The transformation \( \hat{e}_i = a_i - a_i^+ \), \( \hat{e}_i^+ = a_i + a_i^+ \) of previous subsection is the simplest case of Bogoliubov’s transformations[61], pages 326-336, 527-537. They are heavily used in condensed matter and nuclear physics theories. Typically, in such theories one writes:
\[
\hat{e}_i = u_i a_i - v_i a_i^+, \hat{e}_i^+ = u_i a_i + v_i a_i^+. \tag{E.4}
\]
subject to the constraint \( u_i^2 + v_i^2 = 1 \). In such a case, one ends up again with the anticommutator \( \{ \hat{e}_i, \hat{e}_j^+ \} = \delta_{ij} \), e.g. see Eq.s (E.2). In physics this is motivated by the desire to make transformations, Eq.(E.4), 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. By selecting between these bundles leads to the assortment of the 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 the book by Jost [35], pages 209, 210, 213-218 as well as in the Appendix D above. This allows us, following [60], to present in this subsection the condensed matter-like derivation of the same results. To this purpose, we select the second quantized Hamiltonian \( \hat{H} \) in the form given on page 528, Eq.(58.63), of Ref.[61]. That is
\[
\hat{H} = \sum_i H_i a_i^+ a_i - \frac{1}{2} \sum_{i,j,k,l} H_{ijkl} a_i^+ a_j^+ a_k a_l. \tag{E.5}
\]
\(^8\)In notations of Jost book [35] and, in view of Eq.s (D.10a), (D.10b), the same results are written as \( d = \varepsilon(\eta_i) \nabla_{\varepsilon_i} \) and \( d^+ = -i(\eta_i) \nabla_{\varepsilon_i} \). Read, please, also the next subsection.
The obtained results allow us to demonstrate that \( \hat{\Delta} \) coincides with the Hodge Laplacian \( \Delta_H \). 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. (D.3). We write: \( \theta(I) = e_{i_1} \wedge \cdots \wedge e_{i_k} \), 
\( I = \{1 \leq i_1 < \cdots < i_k \leq n\} \). Using Eqs. (D.10a), (D.10b) it is clear that
\( a^+_i \theta(I) \rightleftharpoons \varepsilon(e_i) \theta(I) \) and \( a_i \theta(I) \rightleftharpoons i(e_i) \theta(I) \). From here, it follows [60] that:

\( \sum a^+_i a_i \theta(I) = n \theta(I) \) and

b) if \( A^* \) is an operator inducing an endomorphism of \( \theta(I) \)

\[ A^* \theta(I) = \sum_{j=1}^{k} (-1)^j e_{i_1} \wedge \cdots \wedge (A^* e_{i_j}) \wedge \cdots \wedge e_{i_k} \]  \hfill (E.6)

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

With these results in our hands and, using the definitions of \( d \) and \( d^+ \), the Hodge Laplacian \( \Delta_H \) acting on \( \theta(I) \) can be presented now as follows:

\[ \Delta_H \theta(I) = - \sum_{k,l} (a^+_k a_l \nabla_k \nabla_l + a_l a^+_k \nabla_l \nabla_k) \theta(I) \]

\[ = - \sum_{k,l} \{a^+_k, a_l\} \nabla_k \nabla_l - a_l a^+_k (\nabla_k \nabla_l - \nabla_l \nabla_k) \theta(I) \]

\[ = (-g^{ij} \nabla_i \nabla_j + \hat{R}) \theta(I). \]  \hfill (E.7)

Here we used Eq. (24). That is, we took into account (see Eq. (E.6)) that
\( (\nabla_k \nabla_l - \nabla_l \nabla_k)(X) = R(X_k, X_l)(X) \), \( R(X_k, X_l) = - \sum_{i,j} R_{ijkl} a^+_i a_j a^+_k a_l \).

And, in view of the second line of Eq. (E.7), it is convenient to define \( \hat{R} = - \sum_{i,j,k,l} R_{ijkl} a^+_i a_j a^+_k a_l \). Since typically \( g^{ij} \) is the diagonal matrix and, since
\( \sum a^+_i a_i \theta(I) = n \theta(I) \), by comparing Eqs (E.5) and (E.7) 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 \( \hat{R} \) in Eq. (E.7) be replaced by the scalar curvature \( R \). This requires more work leading to the assortment of the W-L formulas. In particular, now we are in the position to write down the 1st W-L formula. Following Ref. [60], the 1st W-L formula is obtained for the Clifford bundle if we are interested in using Eq. (E.7) acting on one forms. In such a case, using Eq. (E.1a) we obtain \( a_j a^+_k = \delta_{jk} - a^+_k a_j \) and then, use it in the definition of \( \hat{R} \). That is we obtain:

\[ - \sum_{i,j,k,l} R_{ijkl} a^+_i a_j a^+_k a_l = \sum_{i, l} R_{i} a^+_i a_l - \sum_{i,j,k,l} R_{ijkl} a^+_i a_k a_j a_l. \]  \hfill (E.8)
Here $R_{il}$ are the components of the Ricci tensor (read below). The last term in Eq.(E.8) naturally produces zero when it is acting on $\theta(I)$ since now it is the one-form. Thus, the 1st W-L formula reads:

$$\Delta_H = \nabla^* \nabla + Ric, \quad (E.9)$$

where $\nabla^* \nabla = -g^{ij} \nabla_i \nabla_j$ and, according to Ref.63, $\text{Ric} = \sum_{il} R_{il} a_i^a a_l$ represents the Ricci tensor. This formula was obtained on the Clifford bundle by Jost [35], page 208, by slightly different method. The detailed derivation of this result using formalism of Clifford algebras is given by Roe [65], page 48. In view of developments presented in the subsection 4, it is appropriate to describe some fine details of Roe’s derivations in this subsection. Thus, we begin with the

**Definition E.1.** Following [62], page 44, we shall 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 is proven [62], pages 46, 47:

**Theorem E.2.** Let $x \rightarrow c(x)$ be a map defined in the Appendix D 1. Let $M$ be a Riemannian manifold and $TM$ its tangent bundle. Then, for any $X, Y$ and $Z \in TM$ we obtain:

$$[R(X, Y), c(Z)] = c(R(X, Y)Z). \quad (E.10)$$

**Definition E.3.** Let $S$ be the Clifford bundle and let $K(e_k, e_l)$ be the *curvature 2-form* (the same as $R(e_k, e_l)$) with values in $\text{End}(S)$. Let $e_i$ be a local orthogonal frame on $TM$. The endomorphism

$$K = \sum_{i<j} c(e_i)c(e_j)K(e_i, e_j) \quad (E.11)$$

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

**Corollary E.4.** Let $\mathcal{D} = d + d^+$ be the Dirac (also, the de Rham operator [62], page 51) operator on the Clifford bundle $S$. Then, the Weitzenbock formula is given by

$$\mathcal{D}^2 = \nabla^* \nabla + K. \quad (E.12)$$

Evidently, Eq.(E.9) is a special case of Eq.(E.12).

**Definition E.5.** On $TM$ the curvature operator $R$ can be presented as well via equation [62], page 47,

$$R(e_i, e_j)e_a = \sum_l R_{laij} e_l, \quad (E.13)$$

where $R_{laij}$ is the 4-component Riemann curvature tensor with respect to the orthogonal frame made of $e_i$’s

**Definition E.6.** The *Riemann endomorphism* $R^S$ of the Clifford bundle $S$ is defined as

$$R^S(X, Y) = \frac{1}{4} \sum_{k, l} c(e_k)c(e_l) < R(X, Y)e_k, e_l > . \quad (E.14)$$
The $\mathcal{R}^S$ is playing central role in the W-L-type calculations. Specifically, by analogy with Eq.(E.10) it is also possible to arrive at \[62\], page 47, 48,
\[ [\mathcal{R}^S(X,Y), c(Z)] = c(R(X,Y)Z). \] (E.15)

The importance of this result can be seen from the Theorem3.16 proven by Roe[62], Theorem E.7. The curvature 2-form $\mathcal{K}$ is given by
\[ \mathcal{K} = \mathcal{R}^S + \mathcal{F}^S \] (E.16)
where $\mathcal{F}^S$ is the twisting curvature of $S$.

Below, in subsection E.4., we are going to demonstrate that the twisting curvature $\mathcal{F}^S$ possesses the property
\[ [\mathcal{F}^S(X,Y), c(Z)] = 0. \] (E.17)

In the same subsection we shall 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). Other two W-L formulas require \[35\] uses of spinor bundles instead of Clifford bundles. This can be understood if we equivalently rewrite $\bar{\mathcal{R}} = -\sum_{i,j,k,l} R_{ijkl} a^+_i a_j a^+_k a_l$ as\[60\]
\[ \bar{\mathcal{R}} = -\frac{1}{16} \sum_{i,j,k,l} R_{ijkl} (\hat{e}_i \hat{e}_j - \hat{e}_i^+ \hat{e}_j^+) (\hat{e}_k \hat{e}_l - \hat{e}_k^+ \hat{e}_l^+) \]
\[ = \frac{\bar{R}}{4} + \frac{1}{8} \sum_{i,j,k,l} R_{ijkl} \hat{e}_i \hat{e}_j \hat{e}_k^+ \hat{e}_l^+. \] (E.18)

The final result is obtained with help of the relation $\hat{e}_i \hat{e}_j - \hat{e}_i^+ \hat{e}_j^+ = -2(a_i^+ a_j + a_i a_j^+)$ and taking into account the symmetry of the Ricci tensor: $R_{ik} = R_{ki}, R_{ik} = R_{ijkj}$. For details, see Ref.[60], pages 70, 71. In Eq.(E.18) $\bar{R}$ is the scalar curvature. The combination $e_i e_j e_k e_l$ is not acting on $\theta(I)$. Instead, it is acting on $S_n$ (defined in Eq.(D.12)), the 2nd term in Eq.(E.18), when acting on these forms produces zero. Thus, the 2nd Weitzenbock-Lichnerovicz formula, associated with Eq.(21d), with $m^2 = 0$, reads as follows
\[ \Delta_H = \nabla^* \nabla + \frac{\bar{R}}{4}. \] (E.19)

It is given on page 218 of Ref.[35], where it was derived differently (read also Roe [62], Proposition 3.18., pages 48-49). Eq.(4) of the main text is obtained with help of the 2nd W-L formula while Eq.(25) is obtained with help of the 3rd W-L formula. Actually, it should be called as Weitzenbock-Lichnerovicz-Schrödinger formula, e.g. Eq.(25), with $m^2 = 0$. It is presented without proof on page 220 of Ref.[35]. This formula is playing the
central role in the S-W theory discussed in section IV.C. To derive this formula requires uses of the concepts of spinor and twisted spinor bundle (for spin$^c$ manifolds). Even though Eq.(25) enters into the S-W theory [37], 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 the special case of this theory. This demonstration is presented below.

### E.3. BCS superconductivity and the Hodge-de Rham theory

In section 5, following Witten [50], we noticed that the S-W equations emerge as generalization of the G-L equations of superconductivity. The microscopic theory of superconductivity was initially developed in Ref.[63] by Bardeen, Cooper and Schriffer (BCS) and, independently, by Bogoliubov [64]. Based on Bogoliubov’s results, Nambu and Jona-Lasino developed a model of elementary particles whose masses were generated dynamically. This had been achieved by superimposing the BCS and the Dirac equation formalism[65]. The detailed derivation of the connection between the BCS and the Dirac formalism is presented as Problem P.3.2, on page 80, in the book [66]. Here, we re derive the same results differently for a reason to be explained in the next subsection.

We begin with Bogoliubov’s results following [67](Lecture 7.3, pages 755-772). Also read [68]. Start with the Hamiltonian, Eq.(E.5), written in the reciprocal k-space as $\hat{H} = \hat{H}_0 + \hat{H}_V$. Here $\hat{H}_0$ stands for one particle Hamiltonian and, $V$ -for the potential energy, that is

$$\hat{H}_0 = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}; \quad \hat{H}_V = \sum_{\mathbf{k}\mathbf{k}'} V^{(0)}_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}'}^\dagger c_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow}. \quad (E.20)$$

The spin index $\sigma$ is assumed to have two values: $\uparrow$ and $\downarrow$. In writing $\hat{H}_V$ only the potential leading to the spin singlet interactions is present since only this potential participates in the superconducting processes. Such written $\hat{H}$ is the Hartree-Fock-type Hamiltonian[68]. The BCS results follow now from the BCS assumption that

$$< c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} > \neq 0. \quad (E.21)$$

Here $< \cdots >$ denotes either the quantum mechanical (zero temperature) or thermal average. Let, furthermore,

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{k}'} V^{(0)}_{\mathbf{k}\mathbf{k}'} < c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} >. \quad (E.22)$$

Then, by applying standard decoupling the effective interaction Hamiltonian $\hat{H}_V^{eff}$ is obtained

$$\hat{H}_V^{eff} = - \sum_{\mathbf{k}} (\Delta_{\mathbf{k}} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} + \Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger). \quad (E.23)$$
Bogoliubov’s contribution lies in observations that: a) the anomalous averages, Eq. (E.21), lead to nonconservation of the total number of particles (method of quasiaverages [13],[14]), b) the Hamiltonian $\hat{H}=\hat{H}_0+\hat{H}^{eff}$ is a quadratic form made of $c$-operators obeying the anticommutation rules, Eq.(E.1a). Bogoliubov noticed that such anomalous (quasi)averages are not typical for superconductivity only. They occur in many branches of solid state physics. They play a pivotal role in this work as well. Use of method of (quasi)averages is resulting in rigorous asymptotically exact solutions of a variety of quantum many-body problems. To deal with the problem b), Bogoliubov proposed to diagonalize the quadratic form $\hat{H}$ via introducing new $\gamma_{k\sigma}$ fermionic operators

$$\begin{align*}
\gamma_{k\uparrow} &= u_k c_{k\uparrow} - v_k c_{-k\downarrow}, \\
\gamma_{k\downarrow} &= u_k c_{k\downarrow} + v_k c_{-k\uparrow},
\end{align*}$$

subject to the standard conditions

$$\{\gamma_{k\uparrow}, \gamma_{k\uparrow}\} = 1, \{\gamma_{k\uparrow}, \gamma_{-k\downarrow}\} = 0, \text{ etc.} \quad \text{(E.25)}$$

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

$$\hat{H} = \sum_{k\sigma} E_k \gamma_{k\sigma} \gamma_{k\sigma}, E_k = \sqrt{\epsilon_k + |\Delta_k|^2}. \quad \text{(E.26)}$$

With these results presented, we are now in the position to rewrite the Hodge-de Rham Laplacian, Eq.(E.8), in the form of Hamiltonian familiar in the solid state physics. From the previous subsection we know that $\sum a_i^+ a_i \theta(I) = n \theta(I)$. Therefore, we are dealing with the Hamiltonian $\tilde{H}$ of the type

$$\tilde{H} = \sum_{ij} [\tilde{g}^{ij} \nabla_i \nabla_j a_i^+ a_j - R_{ij} a_i^+ a_j], \quad \text{(E.27)}$$

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.(E.26), except that $\tilde{E}_k \neq E_k$. The question arises: Under what conditions $\tilde{E}_k$ will look the same as $E_k$? 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 creation and annihilation operators for positrons (holes). At first look, use of these operators in the present context looks permissible but artificial. In the next subsection we shall 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

$$\{b_i, b_j^+\} = \delta_{ij}, \quad \{b_i, b_j\} = 0, \{b_i^+, b_j^+\} = 0. \quad \text{(E.1b)}$$
and impose the additional anticommutator relations
\[ \{a_i, b_j\} = \{a_i, b_j^+\} = \{a_i^+, b_j\} = \{a_i^+, b_j^+\} = 0. \tag{E.1c} \]

Next, we assume that the metric $\tilde{g}^{ij}$ in Eq.(E.27) is diagonal and write instead of Eq.(E.27),
\[ \tilde{H} = \sum_i [\epsilon_i a_i^+ a_i - \epsilon_i b_i^+ b_i] - \sum_{ij} [R_{ij} a_i^+ b_j + R_{ij} b_i^+ a_j]. \tag{E.28} \]

In writing Eq.(E.28) 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 the holes are fermions below the Fermi surface.

Taking into account the anticommutation relations, Eq.s(E.1a)-(E.1c), it is clear that the quantum system as a whole totally decouples so that it is sufficient to consider the diagonalization of the following matrix
\[ M = \begin{pmatrix} \epsilon & -R \\ -R & -\epsilon \end{pmatrix} \tag{E.29} \]
resulting in the eigenvalues $E = \pm \sqrt{\epsilon^2 + R^2}$ coinciding with those in Eq.(E.26). The obtained result is in agreement with the result of Nambu and Jona-Lasono\[65\].

Just obtained result demonstrates that Bogoliubov’s method of quasianverages \[13\],\[14\] resulting in obtaining of 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 3rd W-L formula, e.g. Eq.(25), paying the central role in S-W theory\[37\].

**E.4. The BCS superconductivity and the S-W theory. Physics of spin$^c$ structures**

From the definitions of Clifford and Spinor bundles, Eq.s(D.13), (D.14a), (D14b), it follows that, the differences between these bundles is the same as the differences between the Lie algebras $so(n)$ and $Spin(n)$ discussed in the Appendix D. $Spin(n)$ is a double cover of $so(n)$. Using this fact, it is helpful to restate the content of Eq.(E.6) as the following (Roe \[62\], Lemma 4.8)

**Theorem E.8.** The Lie Algebra $Spin(n)$ can be identified with with the vector subspace of $Cl(n)$ spanned by the products $e_i e_j, i \neq j$. The identification associates the antisymmetric matrix $A_{ij}$ with the element $\frac{1}{4} \sum_{i,j} A_{ij} e_i e_j \in Cl(n)$. It can be demonstrated that, $A_{ij} = 2(\delta_{i1} \delta_{j2} - \delta_{i2} \delta_{j1})$.

Using the 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 2-form, whose matrix entries are $(Re_k, e_i)$, where $R$ is the Riemann curvature operator, e.g. see Eq. (E.13).

With help of Theorem E.8. we now obtain,

$$K = \frac{1}{4} \sum_{i,j} (Re_k, e_i)e_ie_j,$$

(E.30)
on the Clifford bundle and,

$$K = \frac{1}{4} \sum_{i,j} (Re_k, e_i)c(e_i)c(e_j),$$

(E.31)
on Spinor bundle. At the same time, use of Eq.s (E.14), (E.16), (E.31), brings us to the conclusion that $K = R^S$ implying that $F^S = 0$.

Corollary E.9. The twisting curvature of $Spin(n)$ bundle is zero.

If this is so, we need to demonstrate now that only on $Spin^c(n)$ manifolds $F^S \neq 0$. We shall demonstrate this using physics results obtained in previous subsection. We begin with the observation that the result, Eq.(E.26), is obtainable if and only if in addition to electrons the system also has positrons (holes). That is the system is charged, electrically neutral and, hence, the Abelian gauge invariant initially. This observation instantly brings up the twisting curvature $F^S$ into play since, according to Eq.(25), only the twisting curvature is associated with charges. Thus, the $Spin^c(n)$ manifolds should be linked with the charged systems. Eq.(E.28) is written for the system of charged fermions. These can be introduced via the set of anticommutators, Eq.s(E.1.a)-(E.1.c). Alternatively, instead of using the 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 -1’s. By analogy with Eq.s(E.1a),(E.1b),(E.1c),(E.2) we introduce the additional operators $\hat{E}(e_i)$ subject to the Clifford algebra commutation constraint

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

(E.32) 

Furthermore, we require that

$$\hat{c}(e_i)\hat{E}(e_j) = \hat{E}(e_j)\hat{c}(e_i), \hat{E}(e_j) \equiv E(e_j),$$

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

(E.33)

Evidently, the operators $\hat{E}(e_j)$ and $\hat{c}(e_i)$ are playing exactly the same role as the operators $a_i$ and $b_i$ introduced in Eq.s E(1.b), E(1.c). In complete analogy with Eq.(E.31), we define the curvature 2-form $F^S$ as

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

(E.34)
At the same time, following [69], pages 54-55, we rewrite $R^S$ as

$$R^S(e_i, e_j) = \frac{1}{4} \sum_{k,l} R_{ijkl} c(e_k) c(e_l).$$  \hfill (E.35)

Taking into account Eq. (E.16), we now obtain:

$$K = R^S(e_i, e_j) + F^S(e_i, e_j) = \frac{1}{4} \sum_{k,l} R_{ijkl} [c(e_k) c(e_l) - E(e_k) E(e_l)]$$

$$= -\frac{1}{4} \sum_{k,l} R_{ijkl} [c(e_k) + E(e_k)][E(e_l) - c(e_l)].$$  \hfill (E.36)

A quick look at the Appendix E 2. allows us to write $c(e_k) \leftrightarrow e_k = a_k - \bar{a}_k$, $E(e_k) \leftrightarrow e_k = a_k + \bar{a}_k$. These results are compatible with the anticommutators Eq.(E.32),(E.33) since Eq.(E.1a) was used for $a_k$'s. Thus, we obtain:

$[c(e_k) + E(e_k)][E(e_l) - c(e_l)] = 4a_k a_l - 4\bar{a}_k \bar{a}_l$. Substitution of this result into Eq.(E.36) brings us back to Eq.s (E.8), (E.9) as required. Moreover, the obtained result is compatible as well with Eq.s(E.28)and (E.29). Now, we are in the position to finish the description of $\text{Spin}^c(n)$ manifolds. In view of the equivalence $c(e_k) \leftrightarrow e_k = a_k - \bar{a}_k$ and, taking into account Eq.s(D.10)-(D.12), just described equivalence can be written also as $c(e_k) \leftrightarrow \varepsilon(w) - i(\bar{w})$ while $E(e_k) \leftrightarrow \varepsilon(w) + i(\bar{w})$. The first operator, $c(e_k)$, is acting on $W$ space defined by Eq.(D.6) while $E(e_k)$ is operating on $\bar{W}$ space defined by Eq.(D.8). Thus, the $\text{Spin}^c(V) \simeq W \otimes \bar{W}$ in accord with [70], page 512, example 11.1.25. In view of Eq.(D.13) this is spinor bundle (such that, actually, $\text{Spin}^c(V) \times S^1 \rightarrow \text{Spin}^c(V)$) in which the associated bundle is made out of elements complex conjugate to that in the principal bundle

E.5. Madelung-anomalous superconducting atoms.
Superconducting density functional theory (SCDFT).
Bogoliubov-de Gennes (BdG) equations

SCDFT has been very successful in predicting superconductivity for a wide variety of materials, in particular, for study of superconductivity in high pressure environments [5],[71]. According to [72], page 9, the BdG equations are completely analogous to the SCDFT since they are straightforwardly recoverable from the SCDFT. According to [73], ch-r 5, the BdG equations are directly connected with (recoverable from) the equations of BCS theory of superconductivity. Therefore, it makes sense to provide here some details by connecting general results, [5],[73], with results of Appendix E.

We begin with observation that the SCDFT is built around the Kohn-Sham (K-S) density functional theory (DFT). Following [5], page 19, we notice that the key K-S equation formally coincides with Eq.(3) of this work. We say ”formally” since Eq.(3) is the Hartree-Fock (H-F) -type of equation in which the potential contains the direct and exchange effects [68] while in the K-S equation the potential contains...
the material-independent exchange-correlation effects in addition[5]. Nevertheless, using conformal transformations described in section 3.3. of [3] it is possible to convert Eq.(3) and, hence, the K-S equation, into the equation looking like our Eq.(4). But then, according to Appendix E.2, such an equation acquires geometrical meaning since it can be obtained with help of the 2nd 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 the Appendix E.4. Surprisingly, only the ingenuity of purely mathematical results presented in [62],[69] allows us to make a connection with the BdG equations. Using Eq.(29), an eigenvalue equation

\[
\begin{pmatrix}
\epsilon & -R \\
-R & -\epsilon
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix}
= E
\begin{pmatrix}
u \\
v
\end{pmatrix}
\]  
(E.37)

is obtained whose eigenvalues are \(E = \pm \sqrt{\epsilon^2 + R^2}\). Such an eigenvalue equation coincides exactly with the BdG Eq.(5.18) of ch-r 5 of [73]. Various space-time 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 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 mathematical physics literature. However, it is still of interest to check if simple symmetry rules for spin\(^c\), defined in section 4.2. are making sense as well. Thus, the purpose of the Appendix F lies in checking if semi intuitive definitions of section 4.2. are working. For this purpose, we believe, use of the following web link webelements.com/uranium/atoms.html is helpful.

In this link "uranium" stands for the element uranium. Any other element is obtained either by writing its name in the link or by using the l.h.s of the web page for uranium, where all other elements are listed. For instance, consider the spin configuration for the Madelung-regular \(7\)N ([He] 2s\(^2\)2p\(^3\)), that is

\[
\begin{array}{c}
\uparrow \downarrow 1s^2 \\
\downarrow \uparrow 2s^2 \\
\uparrow \uparrow \uparrow \uparrow \uparrow 2p^3
\end{array}
\]  
(F.1)

From the web link, just given, the levels 1s and 2s are visibly below 2p. Evidently, in the absence of magnetic field there is spin degeneracy: all "up" spins can be made "down." Not surprisingly, this atom is diamagnetic, just like the hydrogen. This is nematic-type degeneracy. But, in addition, there is a permutational symmetry. For \(7\)N the electrons at 2s level are entangled by the Pauli principle. If one of them is "up" another must be "down". Both can be permuted with electrons at 2p level where they are all indistinguishable. Such permutations are representing the additional symmetry. Whenever there is an additional permutational symmetry the atom is Madelung-regular.
Incidentally, Li, Na, Ka, Rb, Cs are all hydrogen-like and all are paramagnetic as noticed already in Section 1.A. Naively, this observation implies that the "up-down" symmetry is lost since in case of H it is manifestly present. This fact is reflected in the periodic table compiled by Madelung [17] who made no comments 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 Zeeman effect, e.g. read https://www.damtp.cam.ac.uk/user/tong/aqm/aqmeight.pdf is telling us that with respect to the static magnetic field all atoms are both paramagnetic (this is caused by the interaction term linear in 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 rest of hydrogen-like atoms are strictly paramagnetic. Apparently, this fact and, may be, also other factors, e.g. rigorous development of perturbational theory for superintegrable systems at both classical and quantum levels, resulted in recent complete recalculation of the results known in physics literature (other than [1, 2], see also [43, 44]). The concept of superintegrability is explained in our work [3]. Ref’s [43, 44] do not include perturbations caused by the relativistic effects. The sources of these corrections are described in this paper. At the chemical level of rigor part of such calculation was performed in [45]. 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. 42Mo. For reader’s convenience the list of all Madelung-exceptional atoms is given in https://en.wikipedia.org/wiki/Aufbau principle Should the Madelung regular rule work, the filling pattern for Mo would be: [Kr] 4d45s2. However, the experiment yields: [Kr] 4d55s1, that is

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\hline
4d^5.
\end{array}
\]  

The levels 4d and 5s are not too distant from each other and, furthermore, the level 4d is higher than 5s! There is an obvious "up-down" symmetry for the 4d level but since 42Mo is paramagnetic, the electron on the 5s level should not be mixed with those on 4d. The electron at the lower 5s level makes 42Mo paramagnetic. This (paramagnetic) property can be easily seen by removing all 5 of 4d electrons from 42Mo resulting in exactly the same electron configuration as for Rubidium. And Rb is paramagnetic. Nevertheless, as for other hydrogenic -like Li, Na, Ka and Cs, the "up-down" spin symmetry is not lost and the paramagnetism is result of all kinds of corrections mentioned above. The case displayed in Eq.(F.1) should be linked with the spin manifold because it has permutational symmetry additional to the "up-down" symmetry. The case displayed in Eq.(F.2) is linked with the spin manifold because the "up-down" symmetry on 4d level is manifest. Exactly the same analysis is applicable to the
Madelung-exceptional \(_{24}\text{Cr}([\text{Ar}] 3d^54s^1)\) and to its "twin," \(_{25}\text{Nb}\). In the case of \(_{24}\text{Cr}\), by stripping it from 5 electrons sitting on the 3d level, we end up with the configuration of paramagnetic Potassium, K. Analogously, for the Madelung-anomalous \(_{25}\text{Nb}\) if we strip it from 4 electrons sitting at the 4d level, then we shall bring the electron configuration to that of paramagnetic Rubidium, Rb. The Madelung-exceptional Copper, Eq.(F.3a), is diamagnetic as well as the Gold since its upper energetic level 3d is being occupied by the "Cooper (BCS-type) paired" electrons analogous to that for the Noble gases. And all noble gases are diamagnetic as the link https://periodictable.com/Properties/A/MagneticType.html demonstrates.

\[
\begin{array}{ccccccc}
\uparrow & 4s^1 & \downarrow & \downarrow & \downarrow & \downarrow & 3d^{10} \\
\end{array}
\]

(F.3a)

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

\[
\begin{array}{cccccccc}
\uparrow & 6s^1 & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & 4f^{14} & 5d^{10}
\end{array}
\]

(F.3b)

The level 5d has the highest energy while the 6s - the lowest. The analysis of the Madelung-exceptional Platinum, Radium and Ruthenium proceeds analogously. It is somewhat trickier though. Consider, for instance, the Ruthenium

\[
\begin{array}{ccccccc}
\uparrow & 5s^1 & \downarrow & \downarrow & \downarrow & \downarrow & 5d^7
\end{array}
\]

(F.3c)

Its analysis proceeds in a very much the same way as that for Mo since, unlike the \(_{23}\text{N}\), whose configuration is displayed in Eq.(F.1), all energies of electrons at 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 that 5s level. The treatment of the remaining Madelung-exceptional Palladium remains is 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 the Madelung-exceptional.

Next, we want to comment on Madelung-exceptional lanthanides (La and Ce) and actinides (Ac and Th). For \(_{57}\text{La}\) the standard Madelung rule prescribes the configuration \([\text{Xe}]4f^15d^66s^2\) while the experiment provides \([\text{Xe}]4f^15d^16s^2\), that is,

\[
\begin{array}{ccccccc}
\uparrow & \downarrow & 6s^2 & 5d^1
\end{array}
\]

(F.4a)

As before, the level 6s is lower than 4f and this level is lower than 5d. \(_{57}\text{La}\) is behaving the same way as the rest of hydrogen-like atoms and, therefore, it is paramagnetic as the rest of them. The electronic configuration of \(_{58}\text{Ce}\) is: \([\text{Xe}]4f^05d^66s^2\). It is paramagnetic, as expected, so that its hydrides should have properties very much analogous to those of \(_{57}\text{La}\). Next, for \(_{89}\text{Ac}\) we have the situation mirroring that of \(_{57}\text{La}\), except that the orbital energy levels are higher: \([\text{Rn}]5f^06d^17s^2\). Finally, for the Thorium,
90\text{Th}, we have: $[\text{Rn}]4f^06d^27s^2$, that is
\[
\begin{array}{ccc}
\uparrow & \uparrow & \downarrow \\
7s^2 & 6d^2 & \\
\end{array}
\]
with 7s energy noticeably lower than 6d so that, again, we have spin$^c$ manifold. We have 90\text{Th} being paramagnetic analogously to all hydrogen-like atoms. It is acting like Madelung-exceptional Rhodium, that is
\[
\begin{array}{cccccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
5s^1 & 4d^8 & \\
\end{array}
\]
All lantanides and actinides are paramagnetic, including Gadolinium, even though another table states that Gd is ferromagnetic.

Finally, let us take a look at the Sulphur, S, whose nonmetallic hydride demonstrated the highest to date $T_c$ under high pressures. For 16\text{S} we have
\[
\begin{array}{cccccccc}
\uparrow & \uparrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
3s^2 & 3p^4 & \\
\end{array}
\]
Eq.(F.5) clearly exhibits the “up-down” and permutational symmetry thus making 16\text{S} Madelung-regular and diamagnetic. Two unpaired electrons make 16\text{S} to act as if it is Madelung-exceptional 90\text{Th}, thus assuring its high temperature superconducting capabilities. These were indeed observed. The difference in the atomic masses positively affected the observed $T_c$'s.

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