How the Modified Bertrand Theorem Explains Regularities and Anomalies of the Periodic Table of Elements

Arkady L. Kholodenko[1]

Department of Chemistry, Clemson University, Clemson, SC 29634-0973, United States

Bertrand theorem permits closed orbits in 3d Euclidean space only for 2 types of central potentials. These are of Kepler- Coulomb and harmonic oscillator type. Volker Perlick recently extended Bertrand theorem. He designed new static spherically symmetric (Bertrand) spacetimes obeying Einstein's equations and supporting closed orbits. In this work we demonstrate that the topology and geometry of these spacetimes permits us to solve quantum many-body problem for any atom of periodic system exactly. The computations of spectrum for any atom are analogous to that for hydrogen atom. Initially, the exact solution of the Schrödinger equation for any multielectron atom (without reference to Bertrand theorem) was obtained by Tietz in 1956. We recalculated Tietz results by applying the methodology consistent with new (different from that developed by Fock in 1936) way of solving Schrödinger's equation for hydrogen atom. By using this new methodology it had become possible to demonstrate that the Tietz- type Schrödinger's equation is in fact describing the quantum motion in Bertrand spacetimes. As a bonus, we solved analytically the Löwdin's challenge problem. Obtained solution is not universal though since there are exceptions of the Madelung rule in transition metals and among lanthanides and actinides. Quantum mechanically these exceptions as well as the rule itself are treated thus far with help of relativistic Hartree-Fock calculations. The obtained results do not describe the exceptions in detail yet. However, studies outlined in this paper indicate that developed new methods are capable of describing exceptions as well. The paper ends with some remarks about usefulness of problems of atomic physics for development of quantum mechanics, quantum field theory and (teleparallel) gravity

Keywords: Maxwell's fish-eye potential, conformally invariant classical and quantum

equations, quantum Bertrand spacetimes, Madelung rule, Einstein-Cartan and teleparallel

gravity

---

[1]Correspondence: string@clemson.edu

Background and summary

Overview of trends in the description of periodic system of elements. Statement of Löwdin's challenge problem

Although quantum mechanical description of multielectron atoms and molecules is considered to be a well established domain of research, recently published book (Thussen and Ceulemans, 2017) indicates that there are still many things which, fortunately, are left for further development. Even though the cited book represents a significant step toward improvement of the existing description of electronic structure of atoms and molecules, we were able to find many items requiring further study. Specifically, the quantum mechanical description of multielectron atom (with atomic number Z and infinitely heavy nucleus) begins with writing down the stationary Schrödinger equation

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

with the Hamiltonian

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

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

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

where $V_{eff}(\mathbf{r}_i)$ is made of the combined nuclear potential - $\frac{Ze^2}{r_i}$ for the i-th electron and the centrally symmetric Hartree-Fock type potential $\mathcal{F}(\mathbf{r}_i)$ coming from the presence of the rest of atomic electrons. The fact that $\mathcal{F}(\mathbf{r}_i)$ is indeed centrally symmetric was discussed in the book by Bethe and Jackiw (Bethe and Jackiw, 2018). It is fundamentally important for our calculations. The symbol $\square_i$ indicates the i-th entry into the set made of hydrogen-like quantum numbers characterizing individual electrons. Recall that the concept of *orbital* is determined by the major quantum number n having its origin in studies of hydrogen atom. The number of electrons allowed to sit on a given orbital is determined by the *Pauli exclusion principle.* Thus, with increasing Z electrons are occupying successive orbitals according to Bohr's Aufbau scheme until the *final ground state electron configuration* is reached. Since electrons are indistinguishable, the hydrogen-like quantum numbers n, l, m and m_s cannot be associated with a particular electron. Therefore, the symbol $\square_i$ should be understood as representing a specific set of quantum numbers otherwise used for description of individual (that is not collectivized)

electrons.The problem with just described *Aufbauprinzip* 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 atom-like wave functions supplying the quantum boxes/numbers $\square_i$ and, b) the Pauli principle which is mathematically restated in the form of the fully antisymmetric wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z)$. Should these requirements be sufficient, then it would be possible with a good accuracy to replace $V_{eff}(\mathbf{r}_i)$ by $-\frac{Ze^2}{r_i}$ so that the filling of electronic levels would occur 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 the problems already for the lithium as explained in the book by Thussen and Ceulemans (Thussen and Ceulemans, 2017), 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 though. Therefore, it was subsequently replaced by the $(n + l, n)$ rule suggested by Madelung- the person who reformulated Schrödinger's equation in hydrodynamic form (Kholodenko and Kauffman, 2018).

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

All the above rules are empirical. As such, they require theoretical explanation. This fact brings us to the

Löwdin's challenge problem: Find a way to derive the Madelung rule ab initio. [2]

The essence of Mendeleev's periodic system of elements lies exactly in discovered periodicity of properties of chemical elements. Although there are 100's of ways this periodicity can be exhibited[3], the commonly accepted periodic table of elements consists of seven periods: 2-8-8-18-18-32-32. Notice that all period lengths occur in pairs (period doubling), except for the very first period of size 2. To determine whether this exception is intrinsic or not, the analysis of work by Charles Janet on periodic table done in 1930 (6 years before work by Madelung!) is the most helpful. It is summarized in the book by Thussen and Ceulemans, pages 336-340. Although initially Janet developed his version of periodic table without guidance of quantum mechanics, eventually he did make a connection with Bohr's results. Janet's periodic table has 8 periods. The periods in Janet's table are characterized (without exception) by the constant value of $N = n + l$ in perfect agreement with the Madelung rule. This fact suggests elevation of the number $N = n + l$ to the rank of new quantum number. By organizing the elements in periods

---

[2]This problem was posed by Per-Olov Löwdin (Löwdin,1969). Additional details and references are in (Allen and Knight, 2002).

[3]Results of www searches indicate that this process is still ongoing.

of constant $n + l$ and 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 apparatus

of the dynamical group theory Thussen and Ceulemans were able to reobtain Janet

sequence. Application of group-theoretic analysis to the periodic system of elements was done repeatedly in the past. Many references to these earlier works can be found in (Thussen and Ceulemans, 2017). To our knowledge, the most notable are results presented in Chapter 6 of the book by Englefield (Englefield,1972). The results of Chapter 6 are independently reobtained in (Thussen and Ceulemans, 2017). Should the Madelung rule be without exceptions, just mentioned results would be sufficient for solving of the Löwdin challenge problem. However, the existing exceptions for transition metals, lanthanides and actinides indicate that use of the dynamical group theory methods alone is not sufficient. As result, in this work we describe alternative methods enabling us to explain the Madelung rule and its exceptions using different physical arguments. This had become possible by elaborating on works by Demkov and Ostrovsky summarized below.

Works by Demkov and Ostrovsky

A concise and convincing explanation of the period doubling and its connection with the Madelung rule is given in (Scerri and Restrepo, 2018). The origins of the Madelung rule had attracted attention of Demkov and Ostrovsky (Demkov and Ostrovsky, 1971). The impact of their work is of major importance for us. Nevertheless, subsequently group-theoretic studies by Kitagawara and Barut (Kitagawara and Barut, 1983) and, later in (Kitagawara and Barut,1984) uncovered the apparent flaws in the logic of Demkov-Ostrovsky calculations. In their book Thussen and Ceulemans (Thussen and Ceulemans, 2017) also expressed their objections to results of the Demkov-Ostrovsky cycle of works. On page 381 of (Thussen and Ceulemans, 2017) we found the following statement:
"Demkov and Ostrovsky developed an atomic physics model that incorporates the Madelung rule, but by replacing the quantization of level energies with quantization of coupling constants at zero energy."

Furthermore, in (Kholodenko and Kauffman, 2019) we noticed that Demkov and Ostrovsky, while being able to obtain correct results, had been unable to provide their rigorous justification because their effective potential $V_{eff}(\mathbf{r}_i)$ was guessed. The authors of the book (Thussen and Ceulemans, 2017) concluded as well that, even though the Demkov -Ostrovsky results do reproduce the Madelung rule correctly, the way these results were obtained cannot be considered as solution of the Löwdin challenge. This circumstance brings us to the following.

Summary of solved problems
General background

4

In (Kholodenko and Kauffman, 2019) we demonstrated that the objections raised in (Thussen and Ceulemans, 2017), (Kitagawara and Barut, 1983) and (Kitagawara and Barut, 1984) are coming from the lack of knowledge of needed mathematical apparatus by the physics and chemistry community, including works by Demkov and Ostrovsly. In mathematical physics community this apparatus is already known in many other contexts. Thus, one of the tasks of this work is to introduce this apparatus to the atomic and molecular physics community. By doing so a number of problems of major importance can be solved so that all of the objections raised in just cited references are removed. Ourselves, we also found some additional objections. They are to be described below and are also removed. This fortunate circumstance is paving a reliable way for subsequent study of exceptions. Detailed results are to be presented in later works.

In their seminal works Demkov and Ostrovsky (D-O) realized that the key to success of solving Löwdin's problem lies is Eq.(2), where $V_{eff}(\mathbf{r}_i)$ should be chosen correctly. The Bertrand theorem of classical mechanics (Goldstein, Poole and Safko, 2014) imposes seemingly insurmountable restrictions on selection of $V_{eff}(\mathbf{r}_i)$ since for spherically symmetric potentials only the Coulombic $-\frac{Ze^2}{r_i}$ and the harmonic oscillator kr^2 potentials allow dynamically closed orbits. D-O believed that, in spite of the indistinguishability of electrons, Bohr's (circular orbits) and, later on, Sommerfeld's (elliptical orbits) treatment of hydrogen atom (Sommerfeld, 1934), is essential for obtaining the discrete spectrum of multielectron atom since the semiclassical-classical methods of treatment of the spectral problem should be associated with closed orbits. At the semiclassical level of description of multielectron atoms the role of closed orbits very recently was discussed, for example in (Akila et al, 2017). Beginning with the classical treatment of motion of electrons in helium, the classical (and, hence, the semiclassical!) dynamics of electrons in multielectron atoms is believed to be chaotic. The seminal book by Gutzwiller (Gutzviller, 1990) is an excellent introduction to this topic. In this work, by developing D-O ideas we argue, that the Madelung rule

is not a reflection of the chaotic dynamics of electrons in multielectron atoms. Instead, it is a reflection of some deep differential geometric and topological properties intrinsic for dynamics of electrons in multielectron atoms. Only the fundamentals are provided

below. The description of mathematical details initiated in (Kholodenko and Kauffman, 2019) is to be extended in future publications.

Arguments leading to extension of the classical Bertrand theorem

Hoping to bypass the limitations of the Bertrand theorem, D-O employed the optical -mechanical analogy in their calculations. It permitted them to use the Maxwell fish-eye potential (and its conformally deformed modifications), e.g. see Eq.(5) below.

The Maxwell fish-eye potential, is used instead of the Coulombic potential for the hydro-gen
atom. Its conformally deformed modification is used instead of $V_{eff}(\mathbf{r}_i)$ for multielectron

atoms. At the level of classical mechanics D-O demonstrated (Demkov and Ostrovsky, 1971) the equivalence (for the hydrogen atom) between the Hamilton-Jacobi equations employing the Maxwell fish -eye and Coulombic potentials. By using the Maxwell fish-eye potential instead of Coulombic, D-O hoped to bypass limitations of the Bertrand theorem. They assumed that the conformally modified fish-eye potential can be used instead of $V_{eff}(\mathbf{r}_i)$ for multielectron atoms. Their work attracted attention of John Wheeler who in (Wheeler,1971), (Wheeler 1976) and, with his student (Powers, 1971), studied classically and semiclassically the electron motion in the fish-eye and conformally deformed fish-eye potentials. The dynamics of electrons in such conformally deformed potentials according to these studies happens to involve orbits which are closed, planar and have self-intersections.In another of his paper (Ostrovsky,1981) Ostrovsky argued that the self-intersections of orbits do not contradict the Bertrand theorem. This statement by Ostrovsky happens to be wrong. Details are explained in (Kholodenko and Kauffman, 2019). Here we provide only very basic arguments.

Classical mechanics treatment of the confined motion of the electron in the Coulombic potential indicates that the motion is planar. Use of the stereographic projection converts the plane into hemisphere as is well known. There could be conversion to the northern or southern hemispheres. Therefore, the plane $\mathbf{R}^2$ with one extra point added (the point at infinity) allows us to identify the plane $\mathbf{R}^2$(with added extra point) and the sphere, S^2. Now, we consider a "trivial" problem: how to describe all closed curves on the sphere? This problem happens to be not as trivial as it looks. It was solved by Little (Little, 1970). He found that there are only 3 distinct regular homotopy classes of oriented closed curves on S^2.These are: a) those for curves without self-intersections, b) those for curves with just 1 self–intersection and, c) those with 2 self-intersections. The b)-type homotopy class curves were obtained by Wheeler (Wheeler,1971). Much more recently, in 2017, the same self-intersecting patterns were obtained for dynamical trajectories existing in Bertrand spacetimes, e.g. see page 3362 of (Kuru et al, 2017). Their results were obtained without any reference to atomic physics or results by Wheeler. The Kepler-Coulomb dynamics in flat 3d Euclidean space does not allow self-intersections. The self-intersections are allowed if the flat space Bertrand theorem is extended to the motions on curved (Bertrand) manifolds (Kuru et al, 2017).

Thus, it follows, that the effects of curvature and the presence of self-intersections in dynamical trajectories are connected to each other.

The sphere S^2 is conformally flat. That is to say, there is a transformation (a conformal transformation, in fact)[4] connecting flat manifolds, e.g. plane $\mathbf{R}^2$, with curved manifolds, e.g. sphere, S^2.**The results of the modified Bertrand theorem are valid exactly for the conformally flat manifolds**. This fact was proven in (Ballesteros, 2009). Thus, flatness of self-intersecting patterns obtained in (Kuru et al, 2017) is, in fact, conformal flatness.

---

[4]It is known that the stereographic projection is such a transformation. Whether or not there are other conformal transformations is of no concern to us in this work.

To connect Bertrand spacetimes with atomic physics we begin with D-O statement made in (Demkov and Ostrovsky,1971). "The Maxwell's fish-eye problem is **closely related to** the Coulomb problem." Being aware of the book by Luneburg (Luneburg, 1966), D-O nevertheless underestimated the nature of connection between the Coulombic and optical (fish-eye) problems described in the book by Luneburg. The assumption of only "close relationship" caused D-O to replace Eq.(3) by

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

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 $V_{eff}(\mathbf{r}_i)$ must be quantized. Such quantization of parameters is making Sturmian and eigenvalue problems equivalent. This circumstance is nontrivial and requires some explanations and examples. These were provided in (Kholodenko and Kauffman, 2019) but were entirely overlooked by D-O. Accordingly, they were also overlooked in (Thussen and Ceulemans, 2017)[5]. Overlooking this circumstance is excusable since it is caused by the gaps in mathematical physics education of physicists and chemists[6].To correct this problem, that is to provide missing details, our readers are encouraged to look into (Kholodenko and Kauffman, 2019). Surprisingly, from this work our readers will find that in many instances use of Eq.(4) is more advantageous than use of Eq.(3). In (Thussen and Ceulemans, 2017), page 377, we read that Eq.(4) "does not describe the bound states of the atom".That this is not the case could be concluded already by D-O themselves should they read the corresponding places in books by Lunenburg (Luneburg,1966) and Caratheodory (Caratheodory, 1937). Ironically, D-O do quote both of these references in (Demkov and Ostrovsky, 1971). This misunderstanding of importance of Eq.(4) and its relation with Eq.(3) resulted in subsequent critique and neglect of D-O works, e.g. read (Thussen and Ceulemans, 2017), page 377. In (Kholodenko and Kauffman, 2019) and papers which will follow later we demonstrate that Maxwell's fish-eye and related to the fish-eye classical and quantum problems are not **closely related to** the Coulombic (hydrogen atom) problems as stated by D-O. Instead, the Maxwell fish-eye problem is **isomorphic** to the Coulombic problem both classically and quantum mechanically. By overlooking the Coulombic-fish-eye isomoprphism at the quantum level D-O argued, nevertheless, that Schrödinger's Eq.(3) with Coulombic and fish-eye-type potentials **both** possess the O(4,2) (or SO(4,2)) dynamical symmetry known for the hydrogen atom (Englefield,1972) and later established for the rest of atoms of periodic table, e.g read (Thussen and Ceulemans, 2017)and references therein. Use of the fish-eye-like potentials by D-O was guided in part by their desire to describe the *atoms other than*

---

[5]E.g. read above in "Works by Demkov and Ostrovsky" subsection.
[6]E.g. read "Summary of solved problems.General background"

hydrogen[7]. In addition, though, they believed that: a)
$V_{eff}(\mathbf{r}_i)$ in Eq.(4) can be represented by the conformally deformed fish-eye potential
because, unlike Eq.(3), Eq.(4) is manifestly conformally invariant[8] so that,
based on arguments presented above, b) use of such (conformally deformed)
potential removes restrictions posed by the Bertrand theorem in flat space.
His paper (Ostrovsky, 1981) Ostrovsky concludes with the following remark:
"It [9] leaves a very interesting question unresolved, the question of why the
interaction of a number of electrons with each other and with an atomic nucleus leads
to an effective one-electron potential having some approximate hidden symmetry.
The method of solution of this question can hardly be envisaged at the present time."
Thus, with formal success of quantum mechanical description of atoms of the whole
periodic system culminating in the formal proof of Madelung rule, Ostrovsky admits
that with all his results published to date, the Löwdin's challenge problem still remains
out of reach. This is so because the deformed fish -eye potential used in D-O calculations
had no visible connection with the $V_{eff}(\mathbf{r}_i)$ coming from the Hartree-Fock calculations.
That is D-O were unaware of such a connection. In addition to their inability to solve
the Löwdin challenge problem, D-O also failed to solve the *Bertrand challenge*[10]:

What makes the deformed fish-eye potential used by D-O as substitute of $V_{eff}(\mathbf{r}_i)$
so good that it removes the restrictions of the classical Bertrand theorem?

Analytical equivalence of the Hartree-Fock $V_{eff}(\mathbf{r}_i)$ and the deformed fish-eye potential. **The place of Bertrand spacetimes in this equivalence**

In their cycle of works on proving the Madelung rule D-O used the fish-eye ($\gamma = 1$) and
conformally deformed ($\gamma \neq 1$) fish -eye potentials

$$V(x,y,z) = -\left(\frac{a}{r}\right)^2 \left[\frac{n_0}{(r/a)^{-\gamma} + (r/a)^{\gamma}}\right]^2, \qquad (5)$$

$r^2 = x^2 + y^2 + z^2, a = const, \gamma$ is a rational number, as an alternative to the $V_{eff}(\mathbf{r}_i)$
Hartree-Fock type potentials routinely used in atomic physics literature. Such a
replacement required them to switch from Eq.(3) to the conformally invariant Eq.(4)
for reasons just mentioned above. More details are provided in (Kholodenko and
Kauffman, 2019). Since Eq.(4) seemingly allows only to look for eigenfunctions
with zero eigenvalue, both D-O and the rest of researchers in the field considered
this limitation as serious deficiency. Based on results of (Kholodenko and
Kauffman, 2019) summarized in previous subsection we claim that, on the contrary,
this restriction is harmless and, in fact, very helpful. Such a replacement of Eq.(3) by

---

[7]Since, as we explained already, D-O believed that by using the fish-eye potential instead of Coulombic it
will become possible to overcome limitations of classical Bertrand theorem applied to multielectron atoms.

[8]Details are explained in (Kholodenko and Kauffman, 2019)

[9]...that is the group-theoretical (our insert from previous discussion) consideration...

[10]Our observation

Eq.(4) was made by D-O for the purpose of taking care of limitations of the classical Bertrand theorem. No other authors, including those performing Hartree-Fock calculations, were concerned with these limitations. In the case of Hartree-Fock type calculations this lack of concern superimpoosed with the fact that $V_{eff}(\mathbf{r}_i)$ is centrally symmetric created a serious problem of deriving and describing semiclassical (and, hence, classical) limit of quantum multielectron models of atoms other than hydrogen. Use of Eq.(4) with potential (5) allowed D-O to neglect works by other authors on the same or related subjects and to draw attention of others to their own works. This happens to be a fundamental drawback causing D-O to acknowledge that, in spite of all their efforts, they still failed to solve the Löwdin problem. D-O realized that when the potential, Eq.(5), used in Eq.(4) the constant n_0 must acquire discrete values as it happens in all Sturmian type problems. Furthermore, for $\gamma = 1/2$ the solution of Eq.(4) provides results compatible with the Madelung rule. The apparent limitation, $E = 0$, along with no apparent relationship between the potential $V(x, y, z)$ and $V_{eff}(\mathbf{r})$ coming from the Hartree-Fock calculations caused Ostrovski to acknowledge (Ostrovsky, 1981) that all D-O results to date do not solve the Löwdin challenge problem. Thus, we are left with the following facts:

a) use of the potential, Eq.(5), apparently removes the limitations of the classical Bertrand theorem;

b) the choice $\gamma = 1/2$ in Eq.(5) apparently consistent with the empirically observed Madelung rule;

c) based on the existing mathematical background of physics and chemistry community, finding of the spectral results beyond $E = 0$ requires use of sophisticated perturbational methods described in D-O works;

d) the choice $\gamma = 1/2$ in Eq.(5) is completely detached from known Hartree-Fock results for $V_{eff}(\mathbf{r})$;

e) the case $\gamma = 1$ corresponds to the standard Maxwell's fish-eye potential. Classical dynamics in such a potential is isomorphic to that in the Kepler-Coulomb potential, that is for the Bohr-Sommerfeld model of hydrogen atom. However, because of the apparent $E = 0$ limitation at the quantum level, neither D-O nor other researchers reproduced known eigenvalue spectrum for the hydrogen atom using Eq.(4).

Subsequently, other authors studied Eq.(4) with D-O potential, Eq.(2), in 2 dimensions where use of conformal transformations leaves Eq.(4) form-invariant. In 3 dimensions one has to use more sophisticated methods of treatments of conformal transformations. These are described in great detail in (Kholodenko and Kauffman, 2019). Form invariance of two dimensional results provides many technical advantages. In spite of this, no attempts to reproduce known 2 dimensional results for hydrogen atom were made till the work by Kholodenko and Kauffman. In (Kholodenko and Kauffmanm 2019) we use the observation (in section 4) that results on $\mathbf{R}^2$ can be lifted to S^2 and then lifted further to S^3 via Hopf mapping. Basic facts on Hopf mapping can be found either in our book (Kholodenko, 2013) or, in condensed form, in (Kholodenko

9

and Kauffman, 2019). Using stereographic projection: from S^3 to $\mathbf{R}^3$, it is possible then to reobtain the D-O results done on $\mathbf{R}^3$. Even though the connection between the Hartree-Fock and the D-O potential, Eq.(5), will be discussed in detail from geometrical and topological perspective in later works, already described results allow us to discuss rigorously some aspects of such a connection now.

Going back to a), we direct our readers attention to the work by Volker Perlick (Perlick, 1992). In it results of the classical Bertrand theorem (Goldstein et al, 2014) valid in Euclidean 3 space had been generalized to static spherically symmetric spacetimes of general relativity. By design, the motion in such curved spacetimes takes place on closed orbits. Detailed calculations performed in (Kholodenko and Kauffman, 2019) demonstrate that the potential, Eq.(5), indeed, removes the limitations of the classical Bertrand theorem since it is actually working not in flat Euclidean $\mathbf{R}^3$ but in curved Bertrand spacetime.

The choice $\gamma = 1/2$ listed in b) and d) is indeed connected directly with results of Hartree-Fock calculations and with Madelung rule. In atomic physics literature the potential, Eq.(5), $\gamma = 1/2$, is known as the Tietz potential. It is bearing the name of his creator. Its origin and many properties are discussed in the book by Flugge (Flugge, 1999). Its remarkable numerical coincidence with the Hartree-Fock type potential $V_{eff}(\mathbf{r}_i)$ was discussed in many places, e.g. read (Kirzhnitz et al,1985), p.664, Fig.10. Tietz, the author who invented the Tietz potential, was initially driven by the desire to simplify the Thomas -Fermi (T-F) calculations. Much more analytically cumbersome T-F type potentials were used by Latter (Latter, 1955) in his numerical study of Schrödinger's equation spectra of low lying excitations for all atoms of periodic system. The numerical results of Latter had been subsequently analyzed by March. On page 76 of his book (March, 1975), without explicit mention of the Madelung rule, March described results by Latter in terms of the Madelung rule.

After discovery of the potential, now bearing his name, Tietz used it in the stationary Schrödinger equation, Eq.(3), in which $V_{eff}(\mathbf{r}_i)$ was replaced by the Tietz potential, that is by Eq.(5) with $\gamma = 1/2$ (Tietz, 1956).Tietz used Eq.(3) in which $E \neq 0$. This is in striking departure from the D-O version of this equation, that is Eq.(4), in which $E = 0$ by design. In the light of results of Appendix F of (Kholodenko and Kauffman, 2019) this happens to be permissible. It is exactly this fact which makes our calculations different from any other performed by standartly trained physical chemists. Unlike Tietz and, in accord with D-O, we used Eq.(4) for solving the corresponding eigenvalue problem. Our method of solving this equation differs from that used by D-O. The fundamental drawback of D-O method of solving Eq.(4) lies in its inability to reproduce the classical hydrogen atom spectrum (problem e)). Therefore, it cannot be considered as reliable and mathematically sound. At the same time, we had began our study of solutions of Eq.(4) by using potential, Eq.(5), with $\gamma = 1$. We succeeded in developing

new method of reproducing hydrogen atom spectrum in 3 dimensions. In addition, we reproduced this spectrum correctly for the 2 dimensional version of the quantum hydrogen atom model as well. Although our method differs from that proposed by Fock in 1936 (Singer, 2005), there is some overlap to be discussed in the next section. Developed method allowed us to bypass entirely the most cumbersome item c) present in D-O works. After solving Eq.(4) with potential, Eq.(5), $\gamma = 1$, correctly, we obtained the low lying spectrum for any atom of the periodic system of elements by employing Eq.(4) with potential, Eq.(5), $\gamma = 1/2$. The obtained results are consistent with the empirical Madelung rule.

Incidentally, Tietz also recognized that Eq.(3) with his potential, that is Eq.(5), $\gamma = 1/2$, can be solved exactly. His first attempt to do exact calculation was made in 1956 (Tietz, 1956).The rest of his attempts is summarized in (Tietz, 1968). Obtained exact solutions differ substantially from those used in D-O works. Besides, Tietz (Tietz, 1956) used his exact solution only to check it against known Hartree-Fock results for the Mercury ($Z = 80$). In doing so he got a very good agreement with published results but never tried to extend the comparison of his exact results for other Z's with those obtained by the Hartree-Fock methods.

Beyond the canonical Madelung rule

General comments

With accuracy of the existing Hartree-Fock methods, including their relativistic versions (Dyall and Faegri, 2007), the question arises: Why one should care about the Madelung rule and its exceptions? To answer this question, we would like to mention the fact, noticed initially by Symanzik (Symanzik, 1966), that all quantum field theories used in particle physics, e.g. those used for description of the Standard Model-an analog of the periodic system at the level of elementary particles, are describable in terms of the models of polymer chains used in polymer physics. More on this is given in the paper by Aisenman (Aisenman,1985), and references therein, significantly developing Symanzik's ideas. The moral of these studies is simple:

instead of building expensive particle accelerators to study physics of elementary particles, it is sufficient to study properties of polymer solutions in the lab. Initially, the (quark model, quark symmetry) ideas of particle physics were used for classification of elements in the periodic system of elements by Fet (Fet, 2016). These were also discussed in some detail in (Thussen and Ceulemans, 2017) and by (Varlamov, 2018) without emphasis on the Madelung rule though. The task of this and future publications is to demonstrate that the noticed fruitful cross-fertilization between just mentioned results of physics and chemistry might potentially yield

new and significant results both in physics and chemistry if the exceptions to the Madelung rule in the atomic physics are to be studied. Below, we initiate such

cross -fertilization process with the following observation

Quantum defects from methods of general relativity and Dirac equation

In 1890 Ridberg conjectured (and tested) that for multielectron atoms the energy spectrum may be written in the form $-\frac{1}{2n^2}$ resembling that for hydrogen atom (Burkhardt and Leventhal, 2006). Since the accidental degeneracy is nonexistent for multielectron atoms the energy is a function of both the principal quantum number n and l is the angular momentum quantum number. Specifically, in the appropriate system of units the energy spectrum for multielectron atoms can be presented as

$$E_{n,l} = -\frac{1}{2(n-\delta_l)^2}. \tag{6}$$

This formula defines the quantum defect δ_l. (Burkhardt et al, 1992) demonstrated that calculation of δ_l can be accomplished in exactly the same way as calculation of the perihelion shift for the Mercury in Einsteinian theory of relativity. In such a case δ_l is proportional to this shift. This fact hints that in the case of multielectron atoms relativistic effects may play an important role. Since in (Kholodenko and Kauffman, 2019) the Madelung rule was obtained within a scope of many-body nonrelativistic quantum mechanics, not surprisingly, a comparison with experimental data indicates that this rule is not universal across the periodic table even though it works rather well for the majority of elements to the extent that some authors, e.g. read chapter 5 of (Scerri and Restrepo, 2018) insisted that, if properly interpreted, the Madelung rule is applicable for the whole periodic system of elements. This fact is supported by the group-theoretic considerations leading to the conclusion that the underlying symmetry of the periodic table is SO(4,2) and, using this symmetry, that the Madelung rule(without exceptions) follows from the group theoretic considerations (Fet, 2016), (Thussen and Ceulemans, 2017), (Varlamov, 2018). Experimental data[11] indicate, nevertheless, that the Madelung rule does have exceptions. All of them are coming from the heavier elements of periodic table. In fact, it is surprising that about 2/3 of elements of the periodic table does obey the Madelung rule in its canonical form[12].
Thus, we are faced with the problem of explaining why at least 2/3 of elements do obey the canonical Madelung rule and what mechanisms break this rule. This problem can be alternatively restated as follows. Why for the most elements of periodic table the relativistic effects are negligible and, why without exceptions, they are significant in the case of elements exhibiting the Madelung

---

[11]https://en.wikipedia.org/wiki/Aufbau_principle
[12]Stated above, in this work.

rule anomalies?

As we just mentioned, theory of quantum defects should, in principle, provide needed answer. But mentioned results based on relativistic calculations known from the theory of theory of perihelion shift are not the only ones which can be used as point of departure. Another approach of computation of quantum defects coming very close to ideas and methods developed in (Kholodenko and Kauffman, 2019) is presented in (Karwowski and Martin,1991) and later, in (Martin, 1997). Both papers use Dirac equation in second order form as point of departure. In its second order form this equation differs very little from the nonrelativistic Schrödinger equation treated in (Kholodenko and Kauffman, 2019). Although not mentioned in just cited works, below we shall argue that calculations based on the perihelion shift (Burkhardt et al 1992) and on use of the Dirac equation (Martin, 1997) are physically not too much different from each other. This fact is of fundamental significance. We shall fully describe it elsewhere.

Phenomenology of the canonical Madelung rule

In previous subsection we noticed that calculations of quantum defect δ_l proceed in complete analogy with those for the perihelion shift in general relativity. This fact indicates that many quantum mechanical features can be explained (visualized) with help of macroscopic phenomena. This was realized already by Darwin shortly after invention of quantum mechanics, e.g. read his book (Darwin, 1931), chapter 5. Darwin used the theory of standing waves (e.g. on the vibrating string) and extended it to two and three dimensions. He did this with the concept of a node.

A node is a point on the string which does not move during the vibration.

When going to two dimensions, nodes are no longer points but lines. E.g. nodal modes of a drum made in a shape of the disc are either radial lines through the disc center or the set of concentric circles around the disc center. Darwin noticed that: "a quick and easy way of describing the various modes, is by taking two numbers, the first of which stands for the number of circular nodal lines and the second for the number of straight radial ones." In the case of three dimensions "*we shall get nodal surfaces instead of nodal lines. These may be either spheres, or else planes or perhaps cones through the centre.*" Just described nodal patterns Darwin connects with the nodal patterns of wave functions for hydrogen atom. His results had been discussed further by Born (Born, 1936), chapter 4. In his book he mentions about *Chladni's figures*. More details/references on these figures are given in (Kholodenko, 2017).These figures can be readily visualized in the case of a circular drum. For this, it is sufficient to cover drum with sand and to make it vibrate. The sand will remain only at the places where there is no vibration. By definition, the fundamental tone exhibits no nodal lines. If these devices are to be compared with the nodal patters of, say, hydrogenic wave functions, the non-vibrating boundary should

be counted as nodal line. This then resolves the apparent difficulty: In the atom, there is no fixed boundary. Instead, there is an atomic nucleus attracting the electron. Wiswesser extended this single electron picture to the multielectron atoms. He also accounted to the Pauli rule in (Wiswesser,1945). Completely independently such a generalization was made in (Steen et al, 2019). In this work all possible droplet motions/vibrations were classified taking into account surface tension acting on the deformable droplet surface. Although Wiswesser was apparently
unfamiliar with the Madelung rule, his way of analyzing nodal patterns of different atoms had lead him to conclude that the nodal patterns consistent with aufbau filing
are possible only if the Madelung rules holding. On page 319 (bottom) of (Wiswesser,1945) we find the statement: "the patterns will be filled in increasing order of $n+l$."
Here n and l were defined in the previous subsection. More specifically, following Darwin's logic, we notice that:
1. Any 3 dimensional nodal pattern is being characterized by 3 numbers a, b and c.
2. Any atomic wave function is characterized by at least 3 quantum numbers n, l and m.
3.The relationship between the numbers a, b and c and n, l and m is given as follows:
$n = a + b + 1$, $l = b$, m may take all integer values between $\pm b$. To extend these rules to multielectron atoms Wiswesser accounted for the spin. His results are summarized in the Table1 of his paper.
Unlike (Wiswesser,1945), the results of (Steen et al, 2019) indicate that:
a) The Madelung-type filling is taking place when $n+l=even$;
b) With increasing n, the Madelung rule becomes irregular.
It is completely useless for us to identify the observed irregularities in the
vibrational patterns of fluid droplets with the exceptions to the validity of the Madelung rule in periodic system. In the next subsection we shall begin explanation why this is so. In the reminder of this section additional details will be added.

The canonical Madelung rule obtained microscopically and its relativization

Since the canonical Madelung rule was obtained microscopically in subsection 4.6 of (Kholodenko and Kauffman, 2019) there is no need to repeat the derivation here. Nevertheless, in this work it is of interest to connect this derivation with phenomenological results of previous section. This connection will also help us to develop the formalism in such a way, that it will become possible to treat the exceptions to the canonical Madelung rule. In doing so we shall initially follow (Kholodenko and Kauffman, 2019), (Englefield,1972) and (Biedenharn and Louck, 1981).
Specifically, in a specially chosen system of units in which the Hamiltonian H for hydrogen atom is dimensionless, it is given in the operator form by

$$\hat{H} = \mathbf{p}^2 - \frac{2}{r} \tag{7}$$

, the Laplace-Runge-Lenz vector $\mathbf{A}_0$ is given by

$$\mathbf{A}_0 = \frac{\mathbf{x}}{r} + \frac{1}{2}(\mathbf{L} \times \mathbf{p} - \mathbf{p} \times \mathbf{L}) \tag{8}$$

14

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

$$\mathbf{A} = \left\{ \begin{array}{c} \mathbf{A}_0(-H)^{\frac{1}{2}} \text{ for E}<0, \\ \mathbf{A}_0 \text{ for E}=0, \\ \mathbf{A}_0 = (H)^{\frac{1}{2}}, \text{ for E}>0. \end{array} \right. \tag{9}$$

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

$$\begin{aligned} \mathbf{J}(\alpha) \times \mathbf{J}(\alpha) &= i\mathbf{J}(\alpha), \alpha = 1, 2 \\ [\mathbf{J}(1), \mathbf{J}(2)] &= 0 \end{aligned} \tag{10}$$

Taking into account that $\mathbf{L}\cdot\mathbf{A}=0$ we also obtain two Casimir operators: $\mathbf{L}\cdot\mathbf{A}=0=\mathbf{A}\cdot\mathbf{L}$ and $\mathbf{L}^2 + \mathbf{A}^2$. The Lie algebras $\mathbf{J}(\alpha) \times \mathbf{J}(\alpha) = i\mathbf{J}(\alpha), \alpha = 1, 2$, are the algebras of rigid rotators for which the eigenvalues $j_\alpha(j_\alpha + 1)$ are known from the standard texts on quantum mechanics. The peculiarity of the present case lies in the fact that $\mathbf{J}(1)^2 = \mathbf{J}(2)^2$. This constraint is leading to the requirement: $j_\alpha = j_\beta = j$. The topological meaning of this requirement is explained in subsection 5.3.3. of (Kholodenko and Kauffman, 2019). In short, the eigenvalue equation for the standard quantum mechanical rigid rotator is that for the Laplacian living on 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 poinwise identification leads to the sphere S^3. Group-theoretically the same result can be stated as $so(4) \simeq so(3) \oplus so(3)$.

With such background we are ready a) to connect the results of previous subsection with those just defined and b) to relativize these results.

We begin with the first task. We proceed by known analogy. The 3 dimensional rigid rotator eigenvalues and eigenfunctions are solutions of the equation

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l + 1)Y_{lm}(\theta, \phi). \tag{11}$$

However $\mathbf{L}^2 = \mathrm{L}_x^2 + \mathrm{L}_y^2 + \mathrm{L}_z^2$ and $\mathrm{L}_x = i\mathrm{D}_{23}, \mathrm{L}_y = i\mathrm{D}_{31}, \mathrm{L}_z = i\mathrm{D}_{12}$, where

$$D_{\alpha\beta} = -x_\alpha\frac{\partial}{\partial x_\beta} + x_\beta\frac{\partial}{\partial x_\alpha}, \quad \alpha < \beta = 1, 2, ...d \tag{12}$$

where d is the dimensionality of space. In 4 dimensions, following (Englefield,1972) we can put $\mathrm{A}_x = i D_{14}, \mathrm{A}_y = i D_{24}, \mathrm{A}_z = i D_{34}$. Thus, if $\mathbf{L}^2$ represents a Laplacian on S^2, the combination $\mathbf{L}^2 + \mathbf{A}^2 \equiv \mathcal{L}^2$ represents a Laplacian on S^3. That is, instead of more familiar (from standard textbooks on quantum mechanics) study of rigid rotator on two-sphere, S^2, the eigenvalue problem for hydrogen atom actually involves study of spectrum of the rigid rotator on 3-sphere. The 3 Euler angles α, θ, ϕ on the 3 sphere are replacing more

15

familiar θ, ϕ angles used for the 2 sphere. The eigenvalue Eq.(11) now is being replaced by

$$\mathcal{L}^2 Y_{nlm}(\alpha, \theta, \phi) = I_{nl} Y_{nlm}(\alpha, \theta, \phi) \tag{14a}$$

This result is almost ready for comparison with that discussed in the previous subsection because in both cases we are having manifestly spherically symmetric wave functions with indices n, l, m. To replace "almost ready" with "ready" we only have to notice that the conformal transformations, e.g. those in Eq.(5), only cause relabeling of the indices in Eq.(14a), e.g. the choice $\gamma = 1$ in Eq.(5) leads to Eq.(14a) (as required for hydrogen atom) while the choice $\gamma = 1/2$ leads to

$$\mathcal{L}^2 Y_{n+l,lm}(\alpha, \theta, \phi) = I_{n+l,l} Y_{n+l,lm}(\alpha, \theta, \phi) \tag{14b}$$

implying the canonical Madelung rule. In (Wiswesser,1945) the relabeling of indices n, m and l was not connected with the Hartree-Fock calculations, etc. and, therefore, cannot be considered as ab initio derivation of the canonical Madelung rule The ab initio proof of this rule is given in (Kholodenko and Kauffman, 2019). Since the canonical rule has exceptions, we are now in the position to relativize the obtained results.

This task requires several steps. First, we notice that in standard 3 dimensional calculations the hydrogen spectrum is determined by the *radial equation*

$$[-\frac{1}{2}(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}) + V(r)]R_{El}(r) = ER_{El}(r). \tag{15}$$

The total wave function $\Psi_E = F_{El}(r)\mathcal{Y}_{lm}(\theta, \phi), \mathcal{Y}_{lm}(\theta, \phi) = r^l Y_{lm}(\theta, \phi), R_{El}(r) = r^l F_{El}(r)$ and $V(r) = -\frac{Ze^2}{r}, m = 1, \hbar = 1$. The combination $F_{El}(r)\mathcal{Y}_{lm}(\theta, \phi)$ can be rewritten in terms of $Y_{nlm}(\alpha, \theta, \phi)$ as demonstrated in (Kholodenko and Kauffman, 2019) and with help of other references therein. Therefore, it is sufficient to look at 3 dimensional results. They can always be mapped onto S^3 using the inverse stereographic projection.

Next, this observation allows us, following Martin and Glauber (Martin and Glauber,1958) and Biedenharn (Biedenharn, 1983), to use the Pauli matrices σ_i in order to rewrite $\mathbf{L}^2 = (\boldsymbol{\sigma} \cdot \mathbf{L})(\boldsymbol{\sigma} \cdot \mathbf{L}+1)$. This identity permits then to write the total momentum $\mathbf{J}$ as $\mathbf{J} = \mathbf{L} + \frac{1}{2}\boldsymbol{\sigma}$. It is convenient then to introduce the operator $\mathcal{K} = \boldsymbol{\sigma} \cdot \mathbf{L}+1$ introduced already by Dirac (Dirac,1958). With help of this operator it is possible to obtain an identity $\mathcal{K}^2 = \mathbf{J}^2 + \frac{1}{4}, \hbar = 1$. The eigenvalues of $\mathcal{K}$ will be denoted by κ. They are: $\kappa = \pm 1, \pm 2, ...$ (0 is excluded). From these definitions it follows that

$$
\begin{aligned}
l &= l(\kappa) = \left\{ \begin{array}{l} \kappa, \text{ if } \kappa \text{ is positive} \\ |\kappa| - 1, \text{ if } \kappa \text{ is negative} \end{array} \right| \\
j &= j(\kappa) = |\kappa| - \frac{1}{2}.
\end{aligned} \tag{16}
$$

The above definitions were made with the purpose not emphasized at all in standard texts on quantum mechanics. Specifically, at the classical level Kepler trajectories can be determined with help of $\mathbf{A}$ only (Collas, 1970). This fact suggests that the quantum analog

of $\mathbf{A}$ should produce the eigenvalue spectrum identical to that obtained from Eq.(15). This is indeed the case. To demonstrate this we introduce the operator $\mathcal{N}$ such that $(\mathcal{N})^2 = (\boldsymbol{\sigma} \cdot \mathbf{A})^2 + (\mathcal{K})^2$. Since it can be shown that $\boldsymbol{\sigma} \cdot \mathbf{A}$ and $\mathcal{K}$ anticommute, it becomes also possible to write

$$\mathcal{N} = \boldsymbol{\sigma} \cdot \mathbf{A} + \mathcal{K} \tag{17}$$

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

$$\boldsymbol{\sigma} \cdot \mathbf{A} \, |N, \varkappa, m> = (N^2 - \varkappa^2)^{\frac{1}{2}} \, | \, N, -\varkappa, m > . \tag{18}$$

It is possible to demonstrate that $N \rightleftarrows E$ with E defined in Eq.(15). With help of this result it is possible to write an exact equivalent of the radial Eq.(15). It is given by

$$[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\mathcal{K}(\mathcal{K}+1)}{r^2} + \frac{2Ze^2}{r} - k^2]F_{N,l(\kappa)}(r) = 0. \tag{19}$$

Here $k^2 = 2|E|, m = 1, \hbar = 1$. Biedenharn (Biedenharn, 1983) explains how the wave function $| N, -\varkappa, m >$ is related to $F_{N,l(\kappa)}(r)$. Also, $\mathcal{K}(\mathcal{K}+1) = l(\kappa)(l(\kappa)+1)$. 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.(15), presented in every textbook on quantum mechanics.

In addition, these results permit relativistic generalization. The control parameter in this generalization is the fine structure constant $\alpha = \frac{e^2}{c\hbar}$. In the limit $\alpha = 0$ the result, Eq.(19), is recovered while for $\alpha > 0$ is replaced by very similarly looking equation[13]

$$[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{\Gamma(\Gamma+1)}{r^2} + \frac{2\alpha ZEe^2}{c\hbar r} - k^2]\Phi_{N,l(\gamma\kappa)}(r) = 0. \tag{20}$$

Here $k^2 = [(m^2c^4 - E^2)/c^2\hbar^2], \Gamma$ is the Lippmann-Johnson operator

$$\Gamma = \mathcal{K} + i\alpha Z\rho_1\boldsymbol{\sigma} \cdot \check{\mathbf{r}}, \tag{21}$$

$\check{\mathbf{r}} = \frac{\mathbf{x}}{r}, \rho_1 \div \rho_3, \sigma_1 \div \sigma_3$ are 4×4 matrices defined in Dirac's book (Dirac,1958). Instead of eigenvalue κ for $\mathcal{K}$ now one has to use $\gamma\kappa$ so that, upon diagonalization, $\Gamma(\Gamma+1) = l(\gamma\kappa)(l(\gamma\kappa)+1)$

and

$$l(\gamma\kappa) = \left\{ \begin{array}{l} \gamma\kappa = \left|\kappa^2 - (\alpha Z)^2\right|^{\frac{1}{2}} \text{ for } \gamma\kappa > 0 \\[2mm] |\gamma\kappa| - 1 = \left|\kappa^2 - (\alpha Z)^2\right|^{\frac{1}{2}} - 1 \text{ for } \gamma\kappa < 0 \end{array} \right. \tag{22}$$

The physical meaning of the factor γ is to be explained in the next subsection. Mathematically, both Eq.s(19) and (20) are looking the same and, in fact, their solution can be reconstructed from the solution of radial eigenvalue Eq.(15) presented in any book on quantum mechanics. The difference lies only in redefining

---

[13]Here, to avoid confusion, when comparing with original sources, we restore $\hbar, c$ and m.

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 in it by $l(\gamma\kappa)$. By replacing l in Eq.(14b) by $l(\gamma\kappa)$ it is immediately clear that the Madelung rule in its canonical form is no longer valid.

Meaning of the γ factor

In previous subsection we provided enough evidence that uses of group theory for derivation of the Madelung rule are destined to fail because standard methods cannot be applied for description of exceptions. We outlined reasons for this to happen by applying accepted rules of both nonrelativistic and relativistic quantum mechanics. In the subsection on quantum defects we mentioned about a peculiar situation of computation of quantum defects purely classically, by analogy with perihelion calculations in general relativity, and purely quantum mechanically, by using theory of relativistic quantum defects. In this subsection we shall describe some fundamental difficulties in formal uses of the existing apparatus of quantum mechanics and general relativity. Atomic physics is the most reliable experimental and theoretical domain of study of possible changes to both quantum mechanics and relativity. This could be seen by studying work by Sommerfeld on fine structure of hydrogen atom.

Sommerfeld wrote his seminal paper on fine structure in 1916 (Granovskii, 2004), the same year Einstein wrote his seminal work on general relativity. To prove correctness of his theory Einstein, in particular, calculated perihelion shift of Mercury (Roseveare, 1982). In writing of his paper Sommerfeld was not driven by this result. He wanted to extend his own results on extension of Bohr's theory of quantized circular orbits. For this purpose he initially extended Bohr's results to describe the elliptic orbits. In Bohr's theory the was only one quantum number, n. Sommerfeld added another two quantum numbers: l and m (Sommerfeld,1934). This was done before 1916. But in 1916 he decided to reconsider his calculations to account for already known effects of fine structure. For this purpose he used the Hamiltonian of the type[14]

$$W = mc^2 - m_0 c^2 - \frac{Ze^2}{r}, \ \ m = \frac{m_0}{\sqrt{1-\beta^2}}, \tag{23}$$

where $\beta^2 = \left(\dfrac{\mathbf{v}}{c}\right)^2$, m_0 is the rest mass of electron, $\mathbf{v}$ is its velocity. Mass of the nucleus is taken to be infinite. By writing the constant angular momentum p_φ as p and by writing $s = \frac{1}{r}$ Sommerfeld obtained the equation for electron's trajectory

$$s(\varphi) = C + A\cos\gamma\varphi \tag{24}$$

where $\gamma^2 = 1 - \frac{p_0^2}{p^2}$, $p_0 = \frac{Ze^2}{c}$. It happens, that just introduced γ is the same as γ in Eq.(22) (Biedenharn, 1983). This fact is fundamental and requires more explanation than

_____

[14]Here we follow notations of Sommerfeld.

given by Biedenharn. First, the electron mass m in Eq.(23) takes care of relativistic effects but the potential term in Eq.(23) is non relativistic. That is it does not take into account the retardation effects. Thus, the modification of the Kepler problem made by Sommerfeld only takes care of the mass which is becoming velocity-dependent. This leads to two fundamental new effects.

a) The Laplace-Runge-Lenz vector is no longer a constant of motion. This fact removes the accidental degeneracy.

b) For $\gamma = 1$ the electron trajectory, Eq.(24), is describing Kepler's elliptic orbits (Landau and Lifshitz, 1960). For $\gamma < 1$ the orbit never closes because of the precession analogous to that calculated by Einstein for Mercury. Sommerfeld being aware of Einstein's result, also calculated the perihelion shift by appropriately choosing constants in Eq.(23), and obtained $7''$ per century. He compared his result with $43''$ obtained by Einstein for the Mercury and came to wrong conclusion that his $7''$ result have nothing to do with general relativity.

But, given that the orbit is not closed, it cannot be quantized! Sommerfeld did not give up,however, in his search in obtaining fine structure spectrum for hydrogen. He noticed that the prihelion shift $\Delta\varphi$ is obtainable as follows: $\Delta\varphi = \frac{2\pi}{\gamma} - 2\pi$. To cope with this shift, Sommerfeld transferred his calculations to the rotating system of coordinates. For this purpose he introduced angle $\psi = \gamma\varphi$ so that eventually the orbit became closed. Application of the Bohr-Sommerfeld quantization prescription had lead him to the fine structure spectrum

$$E(n_r, n_\varphi) = m_0 c^2 (1 + \frac{\alpha^2}{\omega^2})^{-\frac{1}{2}}, \qquad (25)$$

where $\omega = n_r + \sqrt{n_\varphi^2 - \alpha^2}$. Exactly the same result[15] was later reobtained by Dirac (Dirac, 1958) with help of Dirac equation. The spectrum was actually obtained by Darwin and Gordon in 1928 (Granovskii, 2004). Neither Dirac nor Sommerfeld had further investigated the remarkable coincidence between Bohr-Sommerfeld-style calculations of the spectrum and truly quantum mechanical claculations. This issue was addressed in (Biedenharn, 1983) and, more recently, in (Keppeler, 2003). Fortunately, these people, have not at all exhausted the topic of this remarkable coincidence.

Challenges for quantum mechanics coming from the effects of gravity

a) Motion on a cone

The result $7''$ per century for relativistic electron in Coulomb (or gravitational) field was obtained already in the work by Poincare' in 1905. This is described in detail in (Provost and Bracco, 2018), immediately after their Eq.(11). Poincare', obtained his result within a scope of relativistic theory of gravity which he developed. Poincare' died in 1912, while the theory of general relativity inaugurated in 1916 provided $43''$.This was one of its major

---

[15]Provided that the meaning of n_r and n_φ is slightly redefined (to account for electron spin)

hallmarks. Accordingly, for almost a century the perihelion problem was considered as closed and Poincare′ gravity results were forgotten. The difficulties with other formulations, e.g. based on Eq.(24) emerged relatively recently. These are noticed for the first time here, in this work. Specifically, in (Al-Hashimi and Wiese, 2008) the authors considered both classical and quantum mechanical dynamics of a particle moving on a cone and bound to its tip by 1/r potential. At the classical level the authors obtained for particle trajectory result identical to our Eq.(24). No attempts to connect this result with that obtained by Sommerfeld was made. Subsequently, the results (Al-Hashimi and Wiese, 2008) had inspired another paper (Brihaye et al, 2014) in which the same problem was studied from the point of view of the validity of the Bertrand theorem. Recall, that the standard Bertrand theorem was obtained for the flat space. The authors intended to extend the validity of this theorem to the conical space. Again, no reference to the work by Sommerfeld was made. By attempting to solve the quantum Bertand problem group-theoretically these authors arrived at the trivial result: γ in Eq.(24) should be an integer for closed trajectories. If the problem is studied traditionally, that is by using the Schrödinger equation, then for the trajectories to be closed γ must be rational. This conclusion was reached in both papers. Further studies of the obtained results indicated that the obtained wave functions exhibit some weird analytical behavior. Not surprisingly, the obtained spectrum drastically differs from that given in Eq.(25). The conical singularities are, in fact, singularities of space-time and their presence makes space-time curved (Kholodenko, 2000), (Al-Hashimi and Wiese, 2008), (Brihaye et al, 2014). Our readers at this point can raise an objection.The Hamiltonian,Eq.(23) involves the Coulombic-type potential. Although analytically both the gravitational and Coulombic potentials look the same, the existing theory of gravity seemingly deals only with modifications of space-time caused by the effects of gravity. This is not the case, however, as it was demonstrated by Rainich (Rainich,1925) and developed subsequently by Misner and Wheeler in a form of geometrodynamics (Misner and Wheeler, 1957). In its original form it had a problem of including spin into theory. Subsequently, the problem was resolved. We included this information, just to demonstrate below, that it is related to our major task of description of the Madelung rule and its anomalies.

b) Problems with special relativity in the light of Sommerfeld results

According to (Misner et al, 1973), chapter 7, Einsteinian special relativity is incompatible with his general relativity. But we just demonstrated that the dynamics involving special relativistic Hamiltonian, Eq.(23), is describing, in fact, dynamics typical for general relativity. The motion originating with help of Eq.(24) is not inertial as required by the rules of special relativity. In the canonical special relativity only frames moving with constant speed are allowed. The motion is taking place with acceleration. And, if this is so, then the form of Hamiltonian, Eq.(24), is questionable (let alone questionable the instantaneity of the Coulombic interaction).
The difficulty is not removed by Sommerfeld's ingenious trick of transforming the

problem into rotating system of coordinates. This transition is essential for quantization but leaves just described problem unsolved. This is so because use of rotating system of coordinates is connected with many issues. At the elementary level the issues are well described by Diecks in (Rizzi and Ruggiero, 2004), chapter 2. The bottom line is the following: as soon as we are in the rotating frame we have to deal with the equivalence principle of general relativity. The use of equivalence principle alone leads us back to the Einsteinian way of calculating the perihelion shift (Roseveare, 1982), chapter 7.7. This then creates a problem with Sommerfeld's calculations of a perihelion shift. Use of rotational system of coordinates is also associated with the Mach principle (Baratini and Christillin, 2012), (Essen, 2013). Thus, we are coming to the conclusion:

Since the Dirac equation is reducible to the Schrödinger equation, it is permissible to use the Dirac equation in both relativistic and nonrelativistic calculations[16].
And if this is so, then the Mach principle of general relativity is essential for quantization of (semi) classical orbits.

That is, contrary to the existing opinions, quantum mechanics and general relativity are inseparable. Influence of effects of general relativity (e.g. post-Newtonian approximation) which begins with the Hamiltonian, Eq.(24), was initiated in the work by Kennedy (Kennedy, 1972). It involves systematic derivation of relativistic corrections routinely used in the relativistic quantum many-body calculations (Dial and Faegri, 2007). These results should be kept in mind when one is thinking about them from the standpoint of a remarkable agreement between results of Sommerfeld and Dirac for the fine structure spectrum. Just mentioned technical difficulties were recognized by Logunov (Logunov,1989) who noticed that the space-time length interval of special relativity is invariant not only with respect to the standard Lorentz transformations used for inertial frames known from any textbook on special relativity but with respect to a much wider set of transformations characteristic for noninertial frames. The question then emerges: what to do with the existing theory of gravitation? Logunov decided to develop new theory of gravitation in which gravity is acting very much like the Maxwell's electrodynamics. Since theory of electrodynamics works perfectly well in Minkovski spacetime, apparently, new theory of gravitation might be also working well in Minkowski spacetime. Although Logunov was able to bring such a theory of gravitation to completion, it was not embraced by others for reasons to be explained. Before explaining, we would like to mention that, in addition to the book by (Rizzi and Ruggiero, 2004), recently, there appeared two other books by Lusanna (Lusanna, 2019) and Gorgoulhon (Gorgoulhon, 2013) discussing special relativity in general frames. Unlike Logunov, these authors stopped short of abandoning the theory of relativity in its classical form. The latest developments in general relativity (to be briefly sketched below) made these books useful only from the historical perspective.

c) Madelung rule and its anomalies explained with help of Schrödinger's

---

[16]This statement will be elaborated futrther below

work on Dirac electron in a gravitational field

The latest developments in general relativity (Aldrovandi and Pereira, 2013) makes theory of teleparallel gravity the most useful. Technically this theory resembles very much Yang-Mills theory whose Abelian and non-Abelian versions are being used for description of all other types of fields. The idea of teleparallel gravity could be traced back, for instance, to 1932[17]. In this year the paper by Schrödinger (Schrödinger, 1932) on Dirac electron in gravitational field was published. Historically, Dirac came up with his equation (Dirac, 1958) being driven by the observation that the standard Schrödinger equation is not Lorentz invariant. Dirac's equation corrects this deficiency. By correcting this deficiency Dirac uncovered spin in 1928. Before, it was artificially inserted into Schrödinger's equation. The idea for doing so belongs 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 and will be discussed further elsewhere. In this paper we only discuss Schrödinger's results in the light of their relevance to the Madelung rule and its anomalies. To squeeze our presentation to a minimum, we follow (Kay, 2020). We begin with the Dirac equation

$$i\gamma^a \partial_a \psi - m\psi = 0 \tag{26a}$$

in which Dirac gamma matrices γ^a obey the Clifford algebra anticommutation rule : $\gamma^a\gamma^b + \gamma^b\gamma^a = 2\eta^{ab}$, $a = 1 \div 4$, η^{ab} is the matrix enforcing the Minkowski signature {1,-1,-1,-1}. As is well known, the equivalence principle of general relativity locally allows us 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 $e^\mu_a(x)e^\nu_b(x)g_{\mu\nu} = \eta_{ab}(x)$.

Thus, the vierbeins carry in themselves the effects of gravity.

To introduce these effects into Eq.(26) can be done as follows. First, the anticommutator $\gamma^a\gamma^b + \gamma^b\gamma^a = 2\eta^{ab}$ is replaced by $\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}$ implying the relationship $\gamma^\mu = e^\mu_a\gamma^a$. The partial derivative ∂_μ is replaced now by the covariant derivative

$$\nabla_\mu \psi = \partial_\mu \psi + \Gamma_\mu \psi, \tag{27}$$

where

$$\Gamma_\mu(x) = -\frac{i}{4}\omega_{ab\mu}(x)\sigma^{ab}; \sigma^{ab} = \frac{i}{2}[\gamma^a, \gamma^b] \tag{28}$$

and

$$\omega^a_{b\mu} = e^a_\nu \partial_\mu e^\nu_b + e^a_\nu e^\rho_b \Gamma^\nu_{\rho\mu}. \tag{29}$$

In the simplest case $\Gamma^\nu_{\rho\mu}$ is the standard Levi-Civita connection determined by the metric tensor $g_{\mu\nu}$. The presence of term $e^a_\nu \partial_\mu e^\nu_b$ in Eq.(29) is responsible for the torsion effects.

---

[17]Actually, it was initiated by Einstein himself a bit earlier but Schrödinger's paper provided some insentive for experimental verification.

These are absent in the canonical general relativity. Extension of general relativity accounting for the torsion effects is known as Einstein-Cartan (ECG) theory of gravity (Hehl et al, 1976). Very accessible (physically illuminating) description of the ECG theory is given in the book (Sabbata and Sivaram,1994), see also (Ruggiero and Tartaglia, 2003). Above, in b), we were concerned with limitations of special relativity. In ECG theory these limitations are removed. Even more so in teleparallel gravity obtainable from ECG theory. Specifically, the Poincare group of special relativity is a semidirect product of Lorentz rotations and translations in 4-space[18]. The mass is connected with translational part of the Poincare'
group while the spin- with its rotational part. In view of this, in ECG it is convenient to associate with the pseudo-Riemannian space V_4 of the canonical Einsteinian gravity the space U_4 made of V_4 and its tangent space associated with every point of V_4[19]. These arguments explain use of Latin (e.g. a,b,..)-for tangent space, and
Greek (e.g. $\mu, \nu, ...$) indices-forV_4, in Eq.s (27-29).Consider now a closed curve in V_4. If one translates tangent vector along a closed curve, after eventual arriving back at the starting point, the vector is not going to point into the same direction as it was pointing initially. If this happens, this is manifestation of curvature of V_4. If one is watching what is happening with the same vector in U_4 one finds that the curve in U_4 is not going to be closed. Furthermore the final direction of the tangent vector is going to be the same as that in V_4. The non closure is associated with torsion. Thus, the effects of curvature can be associated with the effects of Lorentz transformation of special relativity (the equivalence principle causes this to happen) while the effects of translation (associated with non closure)-with torsion. If in canonical gravity (Misner et al, 1973), chapter 7, the Einsteinian special relativity happens to be incompatible with canonical general relativity, in ECG theory there is no need to worry about a variety of frames. All frames could be equally used. With such a background we are ready to discuss further Schrodinger's paper of 1932. The key element which we supply without proof is the identity

$$\left(\nabla_\alpha \nabla_\beta - \nabla_\beta \nabla_\alpha\right)\psi = \frac{1}{8} R_{\alpha\beta\delta\eta}\gamma^\delta\gamma^\eta\psi. \tag{30}$$

Here $R_{\alpha\beta\delta\eta}$ is the Riemannian curvature tensor. Since use of Eq.(27) converts flat space Dirac Eq.(26a) into that in curved space

$$i\gamma^a\nabla_a\psi - m\psi = 0, \tag{26b}$$

[18]E.g. read the Poincare Group in wikipedia

[19]This is very much the same as considering an orthogonal frame of tangent Serret-Frenet vectors moving along a curve. The vectors are moving in Euclidean space associated with orthogonal frame while the curve is having its local curvature and torsion and could live in non Euclidean space

we can consider instead of Eq.(26b) the following equation

$$
\begin{aligned}
0 &= (-i\gamma^\mu \nabla_\mu \psi - m\psi)(i\gamma^\nu \nabla_\nu \psi - m\psi) \\
&= \gamma^\mu \gamma^\nu (\nabla_\mu \nabla_\nu + \nabla_\nu \nabla_\mu + \nabla_\mu \nabla_\nu - \nabla_\nu \nabla_\mu + m^2)\psi \\
&= (g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \frac{1}{8}R_{\alpha\beta\delta\eta}\gamma^\mu \gamma^\nu \gamma^\delta \gamma^\eta)\psi
\end{aligned}
\tag{31a}
$$

obtained with use of $\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}$ and Eq.(30). The above equation can be further rearranged (Moore, 1996) yielding the equivalent final result

$$
\left(g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \frac{R}{4}\right)\psi = 0.
\tag{31b}
$$

As it was demonstrated in (Kholodenko and Kauffman, 2018) the mass term is not essential and can be eliminated by the appropriate substitutions. In (Kauffman and Kholodenko, 2019), sections 3 and 5, we demonstrated that Eq.(31b) (with $m = 0$) is exactly equivalent to Eq.(4). Moreover by choosing the potential, Eq.(5), (with $\gamma = 1/2$) in Eq.(4) provides the solution to Löwdin's challenge problem, that

is establishes the ab initio validity of the canonical Madelung rule. The obtained result, Eq.(31b), is incomplete though. To make it complete, following (Schrödinger, 1932) we have to modify definition of the covariant derivative in Eq.(27) that is to replace $\nabla_\mu = \partial_\mu + \Gamma_\mu$ by $\nabla_\mu = \partial_\mu + \Gamma_\mu - ieA_\mu$ where A_μ is some kind of a vector (e.g. electromagnetic) potential. With such a replacement Eq.(31b) must be substituted by

$$
\left(g^{\mu\nu}\nabla_\mu \nabla_\nu + m^2 + \frac{R}{4} + \frac{ie}{2}\sigma^{ab}F_{ab}\right)\psi = 0; F_{ab} = \partial_a A_b - \partial_b A_a.
\tag{32}
$$

This is the final result obtained by Schrödinger (up to signs and factors i and e). These factors can be correctly restored, e.g. by consulting (Berestetskii et al, 1982) page120, Eq.(32.6). Previously obtained Eq.s(20) and (21) can be related to Eq.s(31b) and (32). Specifically, by putting the fine structure constant α in the Lippmann-Johnson operator to zero we are effectively arriving at Eq.(31b). For nonzero α we have to use Eq.(32).

Conclusions

In this work we demonstrated that ab initio solution of the Madelung rule problem cannot be made just with help of group-theoretic methods. The existing Madelung rule and its exceptions can be detected with help of the well developed to date Hartree-Fock calculations. However, the Madelung rule and its exceptions carry much more information than required for its uses in chemistry. Recall that the invention of quantum mechanics in 1925-1926 was driven by the needs of atomic physics initially. Subsequently, quantum mechanics was extended to quantum field theory resulting in design of the Standard Model of particle physics. It

is exact analog of the periodic system of chemical elements[20]. Not surprisingly, methods of particle physics had been recently applied back to periodic system of elements (Fet, 2016),(Varlamov, 2018).

Einstein was not happy with the formalism of quantum mechanics, mainly because this formalism did not have room for his general relativity formalism. In this work we demonstrated, that the Madelung rule and its exceptions could be used for further development of quantum mechanical formalism because this rule and its exceptions are explicable by a delicate blending of the formalism of quantum mechanics and theory of gravitation, especially in its latest form of teleparallel gravity. We hope, that our work may stimulate further research in the atomic, nuclear, particle and gravitational physics.

References

Allen, l., Knight, E. (2002). The Löwdin challenge. Origin of the $n + l, n$ (Madelung) rule for filling the orbital configurations. *Int.J.Quantum Chemistry* **90,** 80-88.doi:10.1002/qua.965

Al-Hashimi, M.,Wiese,U. (2008) Runge-Lentz vector, accidental SU(2) symmetry, and unusual multiplets for motion on the cone. *Ann.Phys.*323, 82-104.

Aldrovandi, R., Pereira, J.(2013). *Teleparallel Gravity* (Springer Science+Business Media Inc.).1-214.

Aisenman, M. (1985). The intersection of Brownian paths as a case study of a renormalization group method for quantum field theory. *Comm.Math.Physics* 97, 91-110.

Akila, M., Waltner, D., Gutkin, B., Braun, P., Guhr, Th.(2017). Semiclassical identification of periodic orbits in a quantum many-body system. *Phys. Rev. Lett.* 118**,** 16410.

Ballesteros, A., Encio, A., Herranz, F. (2009). Hamiltonian systems admitting a Runge–Lenz vector and an optimal extension of Bertrand's theorem to curved manifolds. *Comm.Math.Phys.* 290**,** 1033-1049. doi: 10.1007/s00220-009-0793-5.

Baratini, L, Christillin, P. (2012). The Machian origin of the centrifugal force. *J.Mod.Phys.* 3, 1298-1300. doi: 10.4236/jmp.2012.329167.

Bethe, H., Jackiw,R. (2018) *Intermediate Quantum Mechanics.* (CRC Press).1-217.

Berestetskii,V., Lifshitz, E.,Pitaevski,L. (1982) *Quantum Electrodynamics.* (Pergamon Press,Ltd.)

Biedenharn, L., Louck, J.(1981) *Angular Momentum in Quantum Physics.* (Addison-Wesley Publ.Co).1-716.

---

[20]https://en.wikipedia.org/wiki/Standard_Model

Biedenharn, L.(1983) The "Sommerfeld puzzle."Revisited and resolved.
Found.Phys. 13, 13-34.

Born, M. (1936) The Restless Universe. (Harper & Brothers Publishers).1-278.

Brihaye, Y., Kosinski, P.,Maslanka P. (2014) Dynamics on the cone: Closed
orbits and superintegrability. Ann.Phys. 344, 253-262.

Burkhardt,Ch., Leventhal, J. (2006). Topics in Atomic Physics.
(Springer Science+Business Media Inc.).1-287.

Burkhardt, Ch., Hezel,T., Ciocca M., L-W.He, Leventhal,J. (1992). Classical view of
the properties of Rydberg atoms: Application of the correspondence principle.
Am.J.Physics 60, 329-335.doi:10.1119/1.16876.

Caratheodory, C. (1937) Geometrische Optics. (Springer, Berlin). 1-104.

Collas, P. (1978). Algebraic solution of the Kepler problem using the Runge-Lentz
vector. Am.J. of Phys.38, 253-255.

Darwin, C. (1931). The New Concepts of Matter. (The McMillan Co.New York).1-224.

Dirac, P. (1958). Principles of Quantum Mechanics. (Clarendon Press, Oxford).1-315.

Demkov,Y., Ostrovsky,V. (1971) Internal symmetry of the Maxwell "fish-eye"
problem and the Fock group for hydrogen atom.
Sov.Phys. JETP 13, 1083-1087.

Dyall, K., Faegri, K. (2007) Introduction to Realativistic Quantum Chemistry.
(Oxford U.Press). 1-518.

Englefield, M. (1972). Group Theory and Coulomb Problem. (Wiley Interscience).1-120.

Essen, H. (2013). The exact darwin Lagrangian. European Physics Lett. 79, 6002.
doi: 10.1209/0295-5075.

Fet, A. (2016). Group Theory of Chemical Elements (de Gryuter, Berlin).1-184.

Flugge, S. (1999). Practical Quantum Mechanics. (Springer-Verlag, Berlin)

Goldstein, H., Poole,C., Safko, J. (2014). Classical Mechanics.
(Pearson Education Limited).1-630.

Gorgoulhon, E. (2013). Special Relativity in General Frames.
(Springer-Verlag,Berlin). 1-770.

Granovskii, Ya. (2004). Sommerfeld formula and Dirac's theory.
Physics Uspekhi 47,523-524.

Gutzviller, M. (1990). Chaos in Classical and Quantum Mechanics.
(Springer-Verlag, Berlin).1-432.

Hehl, F., Heyede,P., Kerlick, G. (1976). General relativity with spin and torsion.
Rev.Mod.Phys. 48, 393-416.

Kay, B.(2020). Editorial note to: Erwin Schrodinger, Dirac electron in the gravitational
field I Gen. Relativity and Gravitation 52(3) ,1-14.
doi: 10.1007/s10714-019-2625-z.

Karwowski, J., Martin, I (1991). Quantum defect orbitals and the Dirac second-order
equation. J.Phys.B. 24, 1539-1542.

Kennedy, F. (1972). Approximately Relativistic Interactions. Am.J.Phys.40(1) 63-74.
doi:10.1119/1.1986448

Keppeler, S.(2003). Semiclassical quantization rules for the Dirac and Pauli equations.
$\quad\quad$ *Ann. Phys.* 304, 40-71.

Kitagawara, Y., Barut, A. (1983) Period doubling in the $n + l$ filling rule and dynamical
$\quad\quad$ symmetry of the Demkov-Ostrovsky atomic model.
$\quad\quad$ *J.Phys.B* 16, 3305-3322.

Kitagawara, Y., Barut, A. (1984). On the dynamical symmetry of the periodic table:
$\quad\quad$ II. Modified Demkov-Ostrovsky atomic model.
$\quad\quad$ *J.Phys B* 17, 4251-4259.

Kirzhnitz, D., Lozovik, Y., Shpatkovskaya, G.(1976). Statistical model of matter.
$\quad\quad$ *Sov.Phys. Uspekhi.* 18, 649-672.

Kholodenko, A. (2000). Use of quadratic differentials for description of defects and
$\quad\quad$ textures in liquid crystals and 2+1 gravity. *J.Geom.Phys.* 33, 59-102.

Kholodenko, A. (2013). *Applications of Contact Geometry and Topology in Physics.*
$\quad\quad$ (World Scientific, Singapore).1-475.

Kholodenko, A. (2017). Probabilistic vs optical interpretation of quantum mechanics.
$\quad\quad$ arXiv:1703.04674.

Kholodenko, A.,Kauffman L. (2018). Huygens triviality of the time-independent
$\quad\quad$ Schrödinger equation. Applications to atomic and high energy physics.
$\quad\quad$ *Ann.Phys.* 390, 1-59.

Kholodenko, A., Kauffman L. (2019). How the modified Bertrand theorem explains
$\quad\quad$ regularities of the periodic table I. From conformal invariance to Hopf
$\quad\quad$ mapping. arXiv:1906.05278.

Kuru, S., Negro, J., Ragnisco, O. (2017). The Perlick system type I: From the algebra
$\quad\quad$ of symmetries to the geometry of the trajectories.
$\quad\quad$ *Phys.Lett. A* 381, 3355-3363.

Landau, L., Lifshitz, E. (1960). *Mechanics.* (Pergamon Press, Oxford).1-170.

Latter, R. (1955). Atomic energy levels for the Thomas-Fermi and Thomas-Fermi-Dirac
$\quad\quad$ potential. *Phys.Rev.* 99, 510-519.

Little, J.(1970). Nondegenerate homotopies of curves on the unit 2-sphere.
$\quad\quad$ *J.Diff.Geom.* 4, 339-348.

Logunov, A.(1989). *The Relativistic Theory of Gravitation.*
$\quad\quad$ (Mir Publishers, Moscow).1-320.

Löwdin, P-O. (1969). Some comments on periodic system of elements.
$\quad\quad$ *Int. J.Quant.Chemistry* 3s, 331-334.

Luneburg, R. (1966). *Mathematical Theory of Optics.*
$\quad\quad$ (U.of California Press, Los Angeles). 1-450.

Lusanna, L. (2019). *Non Inertial Frames and Dirac Observables in Relativity.*
$\quad\quad$ (Cambridge U.Press, Cambridge).1-325.

March, N. (1975). *Self-Consistent Fields in Atoms.*(Pergamon Press Ltd.).1-235.

Martin, I. (1997). The relativistic quantum defect orbital methods and some of its
$\quad\quad$ applications. *Molecular Engineering* 7, 51-65.

Martin,P., Glauber, R. (1958). Relativistic theory of radiative orbital electron capture.

Physical Review 109, 1307-1325.

Misner,C., Wheeler, J. (1957) . Classical physics as geometry. *Ann.Phys.*2, 525-603.
doi:10.1016/0003-4916(57)90049-0.

Misner, C., Torn, K., Wheeler, J. (1973). *Gravitation* (Princeton U.Press, Princeton).
1-1275.

Moore, J. (1996). *Lectures on Seiberg-Witten Theory.* (Springer-Verlag, Berlin).1-105.

Ostrovsky,V.(1981). Dynamic symmetry of atomic potential.
J.Phys. B 14**,** 4425-4439.

Perlick,V. (1992). Bertrand Spacetimes. *Class.Quantum Grav.* 9,1009-1021.

Powers, R. (1971). Frequencies of radial oscillation and revolution as affected by features
of a central potential.
Atti del Convegno Mendeleeviano, pp 235-242.

Provost, J-P., Bracco, C. (2018). Lorentz's 1895 transformations, Einstein's
equivalence principle and the perihelion shift of Mercury.
*Eur.J.Phys.*39, 065602. doi: 10.1088/1361-6404/aad75d.

Rainich, G. (1925). Electrodynamics in general relativity theory.
AMS Transactions 27, 106-136.

Rizzi, G, Ruggiero, L. (2004). *Relativity in Rotating Frames.*
(Kluwer Academic Publishers, Boston).1-452.

Roseveare, N. (1982). *Mercury's Perihelion. From Le Verrier to Einstein.*
(Clarendon Press, Oxford). 1-208.

Ruggiero, M., Tartaglia, A. (2003). Einstein–Cartan theory as a theory of defects in
space–time. *Am.J.Phys.*71, 1303-1312. doi:10.1119/1.1596176

SabbataV., Sivaram,C. (1994). *Spin and Torsion in Gravitation.*
(World Scientific, Singapore).1-155.

Scerri, E., Restrepo,G. (2018) *Mendeleev to Oganesson: A Multidisciplinary Perspective
on the Periodic Table.* (Oxford University Press).1-315.

Schrodinger, E.(1932). The Dirac electron in a gravitational field I.
Sitzunsber.Preuss.Acad.Wiss. Phys.Math. K1 105.

Singer,S.(2005).*Linearity, Symmetry and Prediction in the Hydrogen Atom.*
(Springer-Verlag, Berlin).1-275.

Sommerfeld, A.(1934). *Atomic Structure and Spectral Lines.*
(Methuen & Co Ltd. London).1-375.

Steen, P.,Chang, Ch., Bostwick, J. (2019). Droplet motions fill a periodic table.
PNAS 116, 4849-4854. doi:101073/pnas.1817065116.

Symanzik, K. (1966). Euclidean quantum field theory. I. Equations for a scalar model.
J. Math. Phys. 7, 510–525.

Tietz, T. (1956). Atomic energy levels for the approximate Thomas-Fermi Potential.
J.Chem.Phys. 25**,** 789-790.

Tietz, T. (1968). Contribution to the Thomas–Fermi Theory.
J.Chem.Phys. 49**,** 4391-4393.

Thyssen, P. and Ceulemans, A. (2017). *Shattered Symmetry.*

(Oxford University Press).1-498.

Varlamov,V.(2018).Group-theoretical description of periodic system
of elements. *Mathematical Structures and Modelling* 2,5-23.
doi: 10.25513/2222-8772.2018.2.5-23.

Wiswesser,W.(1945). The periodic system and atomic structure.
Journal of Chemical Education 22, 314-322.
doi:10.1021/ed022p314.

Wheeler, J.(1971). From Mendeleev's atom to the collapsing star.
Atti del Convegno Mendeleeviano, pp 189-233.

Wheeler, J.(1976). Semi-classical analysis illuminates the connection between
potential and bound states and scattering. *Studies in
Mathematical Physics(Princeton U.Press).* pp. 351-422.