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The Madelung rule, Regge-like sequences and the conformal Lie algebra

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Abstract. The two main group theoretical models related to the Periodic System of Chemical Elements are reviewed, in connection with the Madelung rule and the construction of orthonormal bases of states for the conformal Lie algebra $\mathfrak{so}(2,4)$. Basing on discrepancies between the Madelung rule and chemical experience, a new approach to the conformal symmetry, currently in development, is described.

1. Introduction

Since its first application in Quantum Mechanics [1], group theory has shown to be a powerful tool to understand and interpret various physical phenomena, from the crystalline structure of solids to the classification of particles and nuclei models. In all these applications, the groups are related usually to the symmetries of the system, either as spectrum-generating or dynamical groups, where the Casimir operators of the corresponding Lie algebra and those of distinguished subalgebras play a central role to describe the system. The usual situation to apply group methods is concerned with classification schemes, where irreducible representations of a Lie group have to be decomposed into irreducible representations of a certain subgroup appearing in some relevant reduction chain. In this context, starting from pioneering work by Pauli and Fock on the Hydrogen atom [2], as well as the important contributions by Racah to atomic spectroscopy using Lie groups [3], the theory has been applied systematically in order to obtain a consistent symmetry scheme of the Periodic System of Elements (PSE in short), providing in such manner a formal background to the otherwise empirical “Aufbauprinzip” popularized by Madelung in the 1930s [4].

In this work, we briefly review some aspects of the group theoretical models proposed in connection with the PSE, specifically the role played by the extended conformal group $SO(2,4)\times SU(2)$ obtained by an ascendant procedure from the geometrical symmetry group $SO(3)$ of angular momentum and the obtainment of orthonormal bases of states for $SO(2,4)\times SU(2)$-multiplets, as well as the so-called Madelung rule, indicating some of the serious shortcomings of the latter in order to be an effective and practical tool in Chemistry (beyond the alkali earths). Even if this prescription is not derivable from the theory, it provides an intuitive interpretation[1]

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[1] In chemical literature this is usually declared as counterproductive, but from the physicist’s point of view,

for the arrangement of elements, as well as a symmetry scheme that has been shown to be of practical use, at least for some special situations. The discussion is finished with a brief overview of a different approach to the conformal symmetry, due to A. Ceulemans and P. Thyssen, based on realizations of Lie algebras in terms of rational functions of enveloping algebras and currently still in progress, for which reason the description is incomplete.

2. Symmetry approaches to the Hydrogen atom and PSE

The symmetry properties of the PSE are directly based on the analysis on geometric and dynamic invariance $SO(3)$ and $SO(4)$ of the Hydrogen atom, from which the symmetry rule is derived as an approximate model. Taking additionally into account the symmetries of the non-relativistic (NR in short) Maxwell equations for classical electrodynamics, this symmetry tower is further enlarged to the conformal group $SO(2,4)$. Finally, the adjunction of spin finally leads to the $SO(2,4)\otimes SU(2)$-models, which constitutes the standard symmetry group considered for the PSE [5, 6]. Actually the conformal group is itself of interest, as it is naturally related to the symplectic group $Sp(8,\mathbb{R})$, corresponding to the dynamical non-invariance group of a four dimensional isotropic harmonic oscillator [7].

We briefly recall the method. For an Hydrogen-like (non-relativistic) atom, we consider the central-field approximation Hamiltonian ($e=\hbar=1$)

$$H = -\frac{1}{2}\frac{\partial^2}{\partial^2 x_\alpha x^\alpha} - \frac{Z}{r}, \tag{1}$$

where $r=\sqrt{x_\alpha x^\alpha}$. It follows at once that the angular momentum components $L_\alpha = \varepsilon_{\alpha\beta\gamma}L_{\beta\gamma} = \frac{-i}{2}\varepsilon\left(x_\beta\frac{\partial}{\partial x_\gamma} - x_\gamma\frac{\partial}{\partial x_\beta}\right)$, as well as $\mathbf{L}^2$, are constants of motion. Additional ones are given by the Runge-Lenz-Pauli vector

$$M = \frac{1}{2}\left(\mathbf{p}\times\mathbf{L} - \mathbf{L}\times\mathbf{p}\right) - Z\frac{\mathbf{r}}{r}. \tag{2}$$

Taken together, the components of these vectors lead to the commutation relations:

$$\begin{aligned}
[L_\alpha, L_\beta] &= \quad i\varepsilon_{\alpha\beta\gamma}L_\gamma,\\
[L_\alpha, M_\beta] &= \quad i\varepsilon_{\alpha\beta\gamma}M_\gamma,\\
[M_\alpha, M_\beta] &= -2iH\varepsilon_{\alpha\beta\gamma}L_\gamma,
\end{aligned} \tag{3}$$

therefore reproducing the structure of a six dimensional Lie algebra whenever the value of H is fixed. It is immediate that this algebra will be semisimple for any non-zero value of H. In addition, the invariant character of the angular momentum and Runge-Lenz components imply the identities

$$L_\alpha M^\alpha = M_\alpha L^\alpha = 0, \quad H = \frac{\mathbf{M}^2 - \mathbf{Z}^2}{2(1+\mathbf{L}^2)}. \tag{4}$$

As known [2], the analysis divides into the following notable cases:

(i) Discrete spectrum: $H<0$.
Considering the change of variable $A_\alpha = \sqrt{\frac{-1}{2H}}M_\alpha$, $J_\alpha = \frac{1}{2}(L_\alpha + M_\alpha)$ and $K_\alpha = \frac{1}{2}(L_\alpha - M_\alpha)$, the brackets in (3) reduce to

$$\begin{aligned}
[L_\alpha, L_\beta] &= i\varepsilon_{\alpha\beta\gamma}L_\gamma,\\
[L_\alpha, K_\beta] &= 0,\\
[K_\alpha, K_\beta] &= i\varepsilon_{\alpha\beta\gamma}K_\gamma,
\end{aligned} \tag{5}$$

symmetry schemes always constitute a guideline.

clearly corresponding to the semisimple Lie algebra $SO(4)$. The corresponding spectrum of the problem is obtained by quantization of the operators $J_3, \mathbf{J}^2, K_3, \mathbf{K}^2$, where $\mathbf{J}^2 = \mathbf{K}^2$ holds. In particular, the eigenvalues (EV in short) $j(1+j)$ of $\mathbf{J}^2$ imply the well known expression

$$E_{2j+1} = -\frac{1}{2}\frac{Z^2}{(2j+1)^2}. \tag{6}$$

It turns out that the energy levels are specified by the representations (j, j) of $SO(4)$.

(ii) Continuous spectrum: $H > 0$.
In this case, the appropriate change of basis is given by $K_\alpha = \sqrt{\frac{1}{2H}}M_\alpha$, from which

$$\begin{aligned} [L_\alpha, L_\beta] &= i\varepsilon_{\alpha\beta\gamma}L_\gamma, \\ [L_\alpha, M_\beta] &= i\varepsilon_{\alpha\beta\gamma}M_\gamma, \\ [M_\alpha, M_\beta] &= -i\varepsilon_{\alpha\beta\gamma}L_\gamma, \end{aligned} \tag{7}$$

corresponding to the structure tensor of the Lie algebra of the Lorentz group $SO(1,3)$. In this case, an analogous reasoning to construct an infinite multiplet of the Lorentz group can be developed.

(iii) Zero energy: $H = 0$. Gives rise to the inhomogeneous group $I\mathfrak{so}(3)$. This symmetry is consistent with the fact that the inhomogeneous algebra is obtained as an Inönü-Wigner contraction of both the $\mathfrak{so}(4)$ and $\mathfrak{so}(1,3)$ Lie algebras.

In any case, the kinetic and potential terms are $SO(3)$ invariant, a fact that is immediately inferred from the structure of the Hamiltonian. Back to the case of the discrete spectrum, the Wigner theorem provides the representations associated to the energy level E_{2j+1}

$$\mathcal{D} = \bigotimes_{l=0}^{n-1}(l), \tag{8}$$

Reducibility of the multiplet is observed whenever $n = 2j + 1 \neq 1$. The discrete spectrum therefore exhibits (accidental) degeneracies of $SO(3)$, and the correct group to be considered is $SO(4)$, as was already observed by Fock [8].

The previous situation for the $N = 3$-Coulomb problem can be formally generalized without difficulty to any arbitrary order $N > 3$, due to the properties of the pseudo-orthogonal Lie groups. Therefore, the groups $SO(N+1)$, $SO(1,N)$ and $ISO(N)$ will emerge as the invariance groups for the discrete, continuous and zero value spectra of N-dimensional Coulomb systems, respectively. Again, the zero energy level arises as a contraction of the orthogonal and pseudo-orthogonal groups. A key point to this symmetry approach is to observe that the chain of geometric and dynamical invariance can be naturally enlarged to the non-invariance dynamical group $SO(2, N+1)$, which for the case of $N = 3$ leads to the conformal group $SO(2,4)$.

Schematically, the chain can be presented as:

$$\begin{tikzcd}
 & SO(1,N) \arrow[dl, "cont"'] \arrow[dr] & \\
I\mathfrak{so}(N) & & SO(2,N+1) \\
 & SO(1+N) \arrow[ul, "cont"] \arrow[ur] &
\end{tikzcd} \tag{9}$$

Equation (9) clearly points out the subgroup chains and symmetry breaking.

3. Analogy between Hydrogen spectrum and PSE

Basing on the central field approximation, various group theoretical models have been developed in order to find a symmetry pattern in the Periodic System of Elements (PSE in short), usually focusing directly on the quantum theoretical approach to the atomic spectra, or some slight variation. Among the different approaches that have been developed in the literature, we briefly comment on two of them, both suggesting a central role of the conformal Lie algebra.

(i) The model based on double-covering group $Spin(4)$, developed in [9], takes the so-called "unitary Coulomb representation" P and defines "chemical states" corresponding to elements.
The main drawbacks of the model are:
  - The representation P is reducible, hence the possibility of accidental degeneracies arises naturally.
  - The disposition of elements with respect to quantum number is not directly related with the underlying symmetry.
  - There is no apparent relation with chemical affinity.

(ii) The Fet-Barut-Konopel'chenko model (short FBK model) proposes a unified treatment of "chemical" and energy spectra based on the extended conformal group $SO(2,4) \times SU(2)$, taking also into account the spin [6, 10]. This approach generalizes naturally the Fock model on $SO(4)$, as well as the geometric invariance $SO(3)$, constituting an "optimal reduction chain". Since $SO(2,4)$ is the largest symmetry group of the (non-relativistic) Maxwell equations [11], the model, in some sense, incorporates the electromagnetic interaction. Although for explicit computation, the group $\widetilde{SO}(2,4) \times SU(2)$ turns out to be a more suitable candidate, the main properties and the quantum numbers, as extracted from the corresponding Lie algebras, remain the same. We will see that this group encompasses the so-called Madelung rule, hence providing and intuitive interpretation of the PSE, even if exactly this fact represents the main drawback of the model, at least when tested for chemical consistency.

In the FBK model, classes of atoms are considered as a multiplet of the group $\widetilde{SO}(2,4) \times SU(2)$, from which an interpretation of the PSE in terms of irreducible representations (short IRREPs) will emerge. The main objective is the construction of an infinite dimensional IRREP R in the Hilbert $\mathcal{H}$ space of two-component Fock functions

$$\psi = \begin{cases} \psi_1(\xi_1, \xi_2, \xi_3, \xi_4) \\ \psi_2(\xi_1, \xi_2, \xi_3, \xi_4) \end{cases} \tag{10}$$

acting on the sphere $\mathbb{S}^3$, thus a Coulomb system. The atoms therefore result from subduced multiplets, and can be identified with properly chosen states in $\mathcal{H}$.
The main features of this symmetry model are :

(i) The basic states are specified by suitable quantum numbers of $\widetilde{SO}(2,4) \times SU(2)$ and the Casimir operators of the reduction chain

$$\widetilde{SO}(2,4) \times SU(2) \supset Spin(4) \supset SU(2)_C \tag{11}$$

(ii) The reduction with respect to the subgroup $SU(2)_C$ provides invariant subspaces R_C^α labelled by $\alpha = (n, \lambda, s_3)$, where n, s_3 are the eigenvalues of group observables and $\lambda(1+\lambda)$ are eigenvalues of the Casimir operator of $SU(2)_C$. An additional quantum number λ is added to separate degeneracies.

(iii) The representation R reproduces, in symmetry terms, those properties derived in the $Spin(4)$-approach.

(iv) A 1-1 correspondence between states $|n, \lambda, \mu, s_3\rangle$ and and eigenvalues for the representation R can be established.

A suitable set of quantum numbers for this model is given by the states

$$|n, \lambda, \mu, s_3\rangle\,, \quad n = 1\cdots\,, \quad \lambda = 0, 1\cdots n-1;\ \mu = -\lambda\cdots\lambda;\ s_3 = \pm\frac{1}{2}. \tag{12}$$

4. The Madelung rule

The so-called Madelung rule [4] is an empirical method that, in spite of its more than contrasted chemical shortcomings, has been useful for the symmetry models based on group theory. This rule is based on the central approximation and the Bohr atomic model, characterizing electrons by the quantum numbers n, l, m. Here l corresponds to the weight of the $(2l+1)$-dimensional representation of $SO(3)$, while m arises from IRREPS of its Abelian subgroup $SO(2)$. Actually, each value of n provides an n^2-dimensional IRREP of $SO(4)$ according to the dimension formula

$$n^2 = 1 + 3 + 5 + ... + n - 1 = \sum_{l=0}^{\frac{n-2}{2}} \dim(l)\,. \tag{13}$$

Within this empirical interpretation, each pair (n, l) corresponds to an atomic shell. According to the "Aufbauprinzip", the energetic increase is related to the reduction chain $SO(4) \rightarrow SO(3)$, which in particular implies that the energy of shells increase by $n+l$, establishing an "energetic" order

$$[1,1] < [2,2] < [3,2] < [3,3] < [4,3] < [4,4] < [5,3] < [5,4] < ..... \tag{14}$$

or $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < \cdots$ in classical spectroscopic notation [12].

l	0	1	2	3	4	5	..
n							
1	[1,1]						
2	[2,2]	[3,2]					
3	[3,3]	[4,3]	[5,3]				
4	[4,4]	[5,4]	[6,4]	[7,4]			
5	[5,5]	[6,5]	[7,5]	[8,5]	[9,5]		
..	..	..	..	..	..	..	..

Each block $[n+l, l]$ is filled with $2(2l+1)$ "elements" with an increasing atomic number Z (left to right), leading to an arrangement

	s	p	d	f	g
$n=1$	1-2				
$n=2$	3-4	5-10			
$n=3$	11-12	13-18	21-30		
$n=4$	19-20	31-36	39-48	57-70	
$n=5$	37-38	49-54	71-80	89-102	121-138
$n=6$	55-56	81-86	103-112	139-152	..
$n=7$	..	..	..	..	..

The interest of the $SO(2,4) \otimes SU(2)$ model in this context is to provide an interpretation of the table and the rule using symmetries, establishing a correspondence with states in some IRREP. To this extent, for any fixed n, the entries of each block are divided according to the principle

- $l=0 \longrightarrow m=-\frac{1}{2},\frac{1}{2}$.
- $l=1 \longrightarrow m=\left\{\left\{-\frac{1}{2},\frac{1}{2}\right\},\quad\left\{-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}\right\}\right\}$
- $l=2 \longrightarrow m=\left\{\left\{-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}\right\}\ ,\left\{-\frac{5}{2},-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2},\frac{5}{2}\right\}\right\}$
- $\cdots$

Now, for any $l \neq 0$, the block is divided into two sectors of $2j+1$ entries; those at the left have the value $j=l-\frac{1}{2}$, while those at the right have the value $j=l+\frac{1}{2}$. The corresponding entries are labelled with $m=-j,\cdots,j$. Following this procedure, each entry corresponds to a state noted $|n,l,j,m\rangle$ of the IRREP

$$R=\bigoplus_{n=1}^{\infty}\bigoplus_{l=0}^{n-1}\bigoplus_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}}(j)=\left[\bigoplus_{n=1}^{\infty}\bigoplus_{l=0}^{n-1}(l)\right]\otimes D_{\frac{1}{2}} \tag{15}$$

of the extended conformal group $SO(2,4)\times SU(2)$.

The previous representation (15) is given over the basis of $SO(2,4)$ obtained from the standard pseudo-rotational basis $L_{\mu\nu}$

$$[L_{\alpha\beta},L_{\gamma\delta}]=i\left(g_{\alpha\delta}L_{\beta\gamma}+g_{\beta\gamma}L_{\alpha\delta}-g_{\alpha\gamma}L_{\beta\delta}-g_{\beta\delta}L_{\alpha\gamma}\right) \tag{16}$$

through the change of basis [11]:

$$\begin{array}{lll}
J_1=\frac{1}{2}\left(L_{14}+L_{23}\right) & J_2=\frac{1}{2}\left(L_{24}-L_{13}\right) & J_3=\frac{1}{2}\left(L_{34}+L_{12}\right)\\
K_1=\frac{1}{2}\left(L_{14}-L_{23}\right) & K_2=\frac{1}{2}\left(-L_{24}-L_{13}\right) & K_3=\frac{1}{2}\left(L_{34}-L_{12}\right)\\
P_1=\frac{1}{2}\left(L_{25}-L_{16}\right) & P_2=\frac{1}{2}\left(-L_{15}-L_{26}\right) & P_0=\frac{1}{2}\left(L_{12}+L_{56}\right)\\
Q_1=\frac{1}{2}\left(L_{25}+L_{16}\right) & Q_2=\frac{1}{2}\left(L_{15}-L_{26}\right) & Q_0=\frac{1}{2}\left(L_{56}-L_{12}\right)\\
S_1=\frac{1}{2}\left(L_{36}-L_{45}\right) & S_2=\frac{1}{2}\left(L_{36}+L_{46}\right) & S_0=\frac{1}{2}\left(L_{34}+L_{56}\right)\\
T_1=\frac{1}{2}\left(L_{36}+L_{45}\right) & T_2=\frac{1}{2}\left(L_{35}-L_{46}\right) & T_0=\frac{1}{2}\left(L_{56}-L_{34}\right)
\end{array} \tag{17}$$

subjected to the linear constraints

$$J_3-K_3-P_0+Q_0=0,\ J_3+K_3-S_0+T_0=0,\ P_0+Q_0-T_0-S_0=0. \tag{18}$$

Among the various possibilities given, a suitable choice for a system of creation and annihilation operators is given by

$$\begin{array}{ccc}
J_\pm=J_1\pm iJ_2, & K_\pm=K_1\pm iK_2, & P_\pm=P_1\pm iP_2,\\
Q_\pm=Q_1\pm iQ_2, & S_\pm=S_1\pm iS_2, & T_\pm=T_1\pm iT_2.
\end{array} \tag{19}$$

This choice of generators is adapted to some of the embedded subgroups relevant to the problem, for example

- $SO(3)\otimes SU(2)$: ladder operators indicate movement for fixed (n,l) and variable (j,m).
- $SO(4)\otimes SU(2)$: fixes n, while the remaining parameters can move.
- $SO(1,2)$: l,j,m fixed, n free.

Here, the number Z is given as function of the various Casimir operators

$$\begin{aligned}
Z &= \frac{1}{6}(n+\ell)[(n+\ell)^2-1]+\frac{1}{2}(n+\ell+1)^2-\frac{1}{4}[1+(-1)^{n+\ell}](n+\ell+1)-4\ell(\ell+1)\\
&\quad +\ell+j(2\ell+1)+m-1.
\end{aligned} \tag{20}$$

Entries in the table are obtained by means of the ladder operators on the vacuum state following the principal chain

$$SO(2,4)\otimes SU(2)\supset SO(4)\otimes SU(2)\supset SO(3)\otimes SU(2)\supset SO(2)\otimes SU(2). \qquad (21)$$

Some structural remarks [2]

- Following this classification, ^{4}He belongs to alkali earth more than to halogens, the latter being specified by triplets $(l,j,m)=\left(1,\frac{3}{2},\frac{3}{2}\right)$.
- The rare earths have a more or less "natural" place within the system, although a displacement in their beginning/end is observed.
- Displacement consistent with the f-shell.[3]
- Predicts a series of "superlanthanides", however positions shifted with respect to the positions suggested by G. T. Seaborg [13].

In all, we should always bear in mind that the conformal group derivation of the PSE is a symmetry scheme whose primary task is to provide an intuitive interpretation of the atomic arrangement. It is not a model developed or derived from experimental data and established to surmount technical difficulties, as is for example the Racah approach to atomic spectra [3]. The conformal group model is developed using a small number of principles, neglecting various fundamental phenomena like orbit-orbit and spin-orbit couplings, hence it cannot be expected to be a faithful description of the periodic system as derived by quantum-chemical methods. The Madelung rule itself is nothing more than an empirical rule, not based on a physical or chemical derivation, but on certain simplified assumptions. The resulting approximation is chemically of interest only for the alkaline earth elements; beyond that point, the anomalies/divergencies observed invalidate the Madelung rule.[4] Some of the deficiencies of the rule are enumerated below [14]:

- The Madelung rule refers to free neutral and unbound atoms. This certainly constitutes a definitive argument against its chemical relevance, as Chemistry is more oriented to the analysis of bonded atoms.
- Implicitly, it is assumed that the electronic configuration of elements is determined by the ground state of the free atom. However, this statement is known to be incorrect for many reasons.
- From the third group onwards, there are divergences of the energetic sequence of orbitals, due to supplementary effects not considered by the rule.
- The Madelung rule is non-relativistic, therefore the relativistic spin-orbit couplings cannot be taken into account. This will inevitably lead to divergencies concerning the ground states.
- The rule does not contemplate or predict the collapse of the PSE from a certain period onwards, as follows from Quantum Mechanics and the stability properties of nuclei [15].

In spite of all these drawbacks, the Madelung rule still has some value, at least as part of a symmetry Ansatz for theoretical Chemistry. Actually it should be mentioned that similar methods have been applied to derive a "periodic system" of molecules, where, at least for the case of diatomic molecules, some useful spectroscopic consequences have been derived [16, 17].

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[2] Compare with the IUPAC classification.

[3] For more details on this point, see the book by B. G. Wybourne cited in [3].

[4] Compare to the usual extrapolation of the quantum chemical approach to the Hydrogen atom and alkaline earths. Again, beyond this point the divergences require correction terms.

4.1. Orthonormal $SO(2,4)$-bases of states and the KGR programm

It is well established fact that a semisimple Lie algebra $\mathfrak{g}$ of rank l has exactly l primitive Casimir operators [18], the eigenvalues of which are useful to distinguish irreducible representations of $\mathfrak{g}$. However, in order to characterize the states within an irreducible representation, $f = \frac{1}{2}(\dim\mathfrak{g} - 3l)$ additional operators (sometimes called Racah operators) are necessary to completely classify states and separate degeneracies. This means that any orthonormal basis of states on $\mathfrak{g}$ should consist of

$$i = \frac{1}{2}(\dim\mathfrak{g} + l) \tag{22}$$

normal operators that are simultaneously diagonalizable. The same number of labels is required whenever we use some subalgebra $\mathfrak{h}$ to label the basis states. While the subgroup provides $\frac{1}{2}(\dim\mathfrak{h} + \mathrm{rank}(\mathfrak{h})) + l'$ labels, where l' denotes the number of invariants of $\mathfrak{g}$ that depend only on variables of the subalgebra $\mathfrak{h}$ [18], in addition to the Casimir operators of $\mathfrak{g}$ we need

$$n = \frac{1}{2}\left(\dim\mathfrak{g} - \mathcal{N}(\mathfrak{g}) - \dim\mathfrak{h} - \mathcal{N}(\mathfrak{h})\right) + l' \tag{23}$$

inner operators (missing label operators) for the separation of states. According to these formulae, for the conformal group $SO(2,4)$ an orthonormal basis of states is determined by 9 commuting operators, three of which correspond to the Casimir operators. In the case of $SO(2,4)$, the suitable orthonormal basis should be constructed with respect to the $SO(4)$ sugbgroup. Using the basis (16), we see that the $\mathfrak{so}(4)$ subalgebra is generated by L_{ij} with $1 \leq i < j \leq 4$. The three Casimir operators C_2, C_4 and C_6 of $\mathfrak{so}(2,4)$ provide three labels, while the Casimir operators C'_{21} and C'_{22} of $\mathfrak{so}(4)$ provide two more. The two internal labels for IRREPs of $\mathfrak{so}(4)$ are determined by the eigenvalues of the Casimir C''_2 of the $\mathfrak{so}(3)$ subalgebra generated by the angular momentum operators, as well as the eigenvalues of the projector L_{13}. This makes 7 labels, and according to (23), we need two more labels to separate the degeneracies. In order to determine them, we decompose the Casimir operators as operators of bi-degree $[a,b]$, i.e., as polynomials of degree a in the variables of the subalgebra $\mathfrak{so}(4)$ and degree b in the remaining generators [19]:

$$\begin{aligned} C_2 &= \Theta^{[2,0]} + \Theta^{[0,2]}, \\ C_4 &= \Theta^{[4,0]} + \Theta^{[2,2]} + \Theta^{[1,3]} + \Theta^{[0,4]}, \\ C_6 &= \Theta^{[6,0]} + \Theta^{[4,2]} + \Theta^{[3,3]} + \Theta^{[2,4]} + \Theta^{[1,5]} + \Theta^{[0,6].} \end{aligned} \tag{24}$$

It can be shown easily that, taking for example the subgroup scalars $\Theta^{[2,2]}$ and $\Theta^{[1,5]}$, we actually have the required commutativity condition $\left[\Theta^{[2,2]}, \Theta^{[1,5]}\right] = 0$. Since these operators commute also with the $\mathfrak{so}(4)$-generators and are independent of the previous seven operators, an orthonormal basis can be given by the eigenvalues of the nine operators $\left\{C_2, C_4, C_6, C'_{21}, C'_{22}, C''_2, L_{13}, \Theta^{[2,2]}, \Theta^{[1,5]}\right\}$.

The KGR programm, first formulated by M. R. Kibler in [20], intends primarily to extend the conformal group approach in quantitative way to describe various properties of atoms, in analogy with the symmetry Ansätze applied in particle physics classification schemes, notably the IBM model. The first step in this direction is to obtain, from $SO(2,4) \otimes SU(2)$ and its more relevant subgroup chains, a set of $9+2$ normal commuting operators that label IRREPs and separate degeneracies. Using the orthonormal basis displayed above for the natural chain $SO(2,4) \supset SO(4) \supset SO(3)$, adding the two labels corresponding to the "spin" subalgebra $\mathfrak{su}(2)$, the implementation of the program reduces to consider linear or functional combinations of these operators and the numerical analysis of their eigenvalues for comparison with various physical properties of atoms, like ionization energies, specific heat or atomic radii. Albeit the problem is formally well established, the main difficulty lies in the numerical part, as the appropriate form of the labelling operators must be determined heuristically from available experimental data, without being based on a theoretical derivation.

5. “Regge” and “Madelung” ladder operators

Another approach to the symmetry scheme of the PSE, based on some observed analogies with the Regge sequences of nuclear physics [21] and currently in progress, has recently been proposed by A. Ceulemans [22]. The main idea of this scheme is the realization of $SO(2,4)$ in terms of creation and annihilation operators that describe diagonal movements in the (n,l) scheme, where the principal diagonal (red) is called the “Regge” sequence, while the counter-diagonal (blue) is called the “Madelung” sequence:[5]

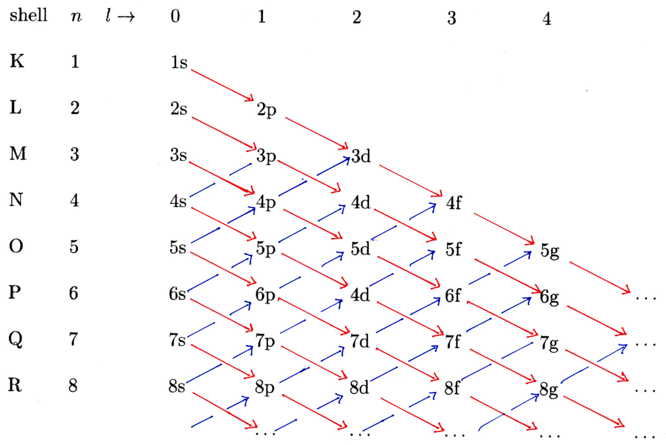

Figure 1. The “Regge” and “Madelung” sequences.

It is clear from this diagram that the classical subgroup chains used in the FBK-model are no longer valid, as both n and l are changed by the action of the creation and annihilation operators. In order to preserve the embedding $SO(3) \subset SO(1,3) \subset SO(2,4)$, it seems plausible to realize the conformal Lie algebra in some enveloping algebra, i.e., considering polynomial generators that reproduce the diagonal movement still preserving angular momentum. Similar constructions have been considered for the Hamilton group in Relativity by means of “virtual” copies of Lie algebras [23].

The first step towards such a realization is a clear identification of the pseudo-rotation generators (16) in terms of their corresponding symmetry subgroups: for $j = 1,2,3$, the generators L_{j4} can be seen as the components of a modified Runge-Lenz vector

$$\mathbf{A} = \frac{1}{2}\mathbf{r}p^2 - \mathbf{p}\,(\mathbf{r}\,\mathbf{p}) - \frac{1}{2}\mathbf{r}, \tag{25}$$

while the generators L_{j5} are identified with the components of a conjugated vector

$$\mathbf{B} = \frac{1}{2}\mathbf{r}p^2 - \mathbf{p}\,(\mathbf{r}\,\mathbf{p}) + \frac{1}{2}\mathbf{r}. \tag{26}$$

The $SO(1,2)$ subgroup is given by L_{46}, L_{45}, L_{56}, renamed as Q_1, Q_2, Q_3 respectively, while the remaining elements L_{j6} are identified with the components of a vector $\mathbf{\Gamma}$ proportional to linear momentum.

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[5] Observe that the latter sequence corresponds to a reversal of the so-called Pauling diagram.

It can be easily seen that the angular momentum generators L and the components of $\mathbf{A}$ span a copy of $\mathfrak{so}(4)$, recovering the chain $SO(2,4) \supset SO(4)$. Further, the L and Q-operators mutually commute and generate a subgroup $SO(3) \otimes SO(1,2)$, providing the chain $SO(2,4) \supset SO(3) \otimes SO(1,2)$. Finally, the L and B-operators span a copy of $SO(1,3)$ (corresponding to the standard and only embedding of the Lorentz algebra.[6]
With these changes, the bound states of the Hydrogen spectrum ($\hbar = 1$), ignoring the spin quantum number s, are still described primarily by the quantum numbers

$$|n\, l\, m\rangle \tag{27}$$

for $n = 1, 2, \cdots$, $l = 0, 1, \cdots$ and $m = -l, \cdots, l$, as specified by the action of the following operators:

$$\mathbf{L}^2\, |n\, l\, m\rangle = l\,(l+1)\; |n\, l\, m\rangle\,; \quad Q_3\, |n\, l\, m\rangle = n\; |n\, l\, m\rangle\,; \quad L_{12}\; |n\, l\, m\rangle = m\; |n\, l\, m\rangle\,. \tag{28}$$

The ladder operators are introduced as linear combinations of the components of the $\mathbf{B}$-vector

$$B_{\pm} = B_x \pm \mathrm{i}\, B_y. \tag{29}$$

As expected, the B_z-operator commutes with L_z and does not change the value of m, while the $B_{\pm}$ satisfy $[L_z, B_{\pm}] = \pm B_{\pm}$ and will raise (lower) the value of m in one unit. Their action on a state shows that we obtain a linear combination of diagonal moves in Figure 1.

$$\begin{array}{rcl} B_z\, |n\, l\, m\rangle & = & \alpha_1\, |n\, -1, l-1,\, m\rangle + \alpha_2\, |n\, +1, l-1,\, m\rangle \\ & & +\alpha_3\, |n\, -1, l+1,\, m\rangle + \alpha_4\, |n+1, l+1,\, m\rangle \\ B_{\pm}\, |n\, l\, m\rangle & = & \beta_{\pm,1}\, |n\, -1, l-1,\, m \pm 1\rangle + \beta_{\pm,2}\, |n\, +1, l-1,\, m \pm 1\rangle \\ & & \beta_{\pm,3}\, |n\, -1, l+1,\, m \pm 1\rangle + \beta_{\pm,4}\, |n\, +1, l+1,\, m \pm 1\rangle\,, \end{array}$$

where α_i, $\beta_{\pm,i}$ are functions depending on n, l, m.
However, in order to have proper diagonal moves as depicted by the "Regge" and "Madelung" sequences, the transformed generators of $SO(2,4)$ are not sufficient. In these conditions, it is convenient to introduce a quadratic operator from the enveloping algebra that allows to discard some of the possibilities for the ladder operators [23]. One possibility is given by an operator S subjected to the constraint $S^2 = \left(L^2 + \frac{1}{4}\right)$. This kind of operator, which can be seen as a "counting operator", was first considered by M. Englefield in the context of spherical harmonics [25]. It turns out that S commutes with the angular momentum subalgebra $SO(3)$ as well as with the radial subgroup $SO(1,2)$, but not with the remaining $SO(2,4)$ generators. The interest of S lies in the possibility of constructing a copy of the Lorentz algebra in the enveloping algebra of $SO(2,4)$, by means of a new vector $\mathbf{K}$ defined by the commutators

$$\begin{array}{rl} K_z & = [B_z, Q_3 + S] \\ K_{\pm} & = [B_{\pm}, Q_3 + S] \end{array} \tag{30}$$

With this modification, the $[L_i, L_j]$ and $[L_i, K_j]$-commutators preserve the usual rules for a $\mathfrak{so}(1,3)$ subalgebra, while the difference is given in the brackets of the $\mathbf{K}$-components:

$$[K_{\pm}, K_z] \sim (Q_3 S^{-1} + 1) L_{\pm}; \quad [K_+, K_-] \sim (Q_3 S^{-1} + 1) L_z. \tag{31}$$

It turns out that $Q_3 - S$ is a constant operator for any Regge-like sequence in Figure 1 and that it appears as a Casimir operator of the Lie algebra generated by the angular momentum and

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[6] Actually this is the origin of introducing additional operators and generalized realizations. This follows easily taking into account the branching rules for the defining representation associated to the embedding [24].

K-generators.
This realization of $SO(1,3)$ can be enlarged, using the generators **A**, **Q** and Γ, to form a Lie algebra isomorphic to the conformal algebra. However, while the usual realization of the conformal algebra as pseudo-rotations clearly indicates the reduction chains and the physical significance of the various generators and subgroups, it is not entirely clear, in this realization in the embedding algebra, how to identify the generators external to the Lorentz subalgebra constructed so far with properties of the Regge sequences and the corresponding symmetry breaking patterns.

6. Comments and Open questions

Some of the group theoretic approaches to the Periodic System of Elements have been reviewed in connection with the empirical Madelung rule. The main shortcomings in the chemical (and physical) context have been described, focusing on the value of the rule as a symmetry scheme that allows to extract orthonormal bases of states. Modification of these are suitable candidates to be used in more realistic descriptions of the PSE, or at least for a more close comparison of experimental data and numerical results derived from either the conformal group model or some generalization. One such possible generalization, based on similarities with reduction chains used in the analysis of nuclei, has been briefly commented. While the realization in the enveloping algebra of $SO(2,4)$ works consistently up to the Lorentz subalgebra, the appropriate interpretation of the remaining generators of the conformal algebra is not clear due to the consideration of the external counting operator S, presenting an obstruction not yet solved. Similar non-linear combinations of $SO(2,4)$ and S-operators allow the description of the "Madelung" sequences in Figure 1, albeit leading to the same obstruction in the interpretation of the realization. It is hoped that this problem, properly contextualized within the frame of non-linear extensions and deformations of Lie algebras [26], will be solved in the near future.

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