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SUMMARY

Some historical facts about the construction of a periodic system of chemical elements are reviewed. The Madelung rule is used to generate an unusual format for the periodic table. Following the work of Byakov. Kulakov. Rumer and Fet. such a format is further refined on the basis of a chain of groups starting with $SU(2) \times SO(4.2)$.

HISTORICAL FACETS

The list of chemical elements has not stopped to grow during the In a schematic way, we have the following last two centuries. guiding-marks (where [xxx, xxx, xxx] stands for [year, number of representative person(s)]): [1789, 23, [1815, 30, Prout], [1818, 40, Berzelius], [1828, 49. Berzelius]. [1849, 61, Gmelin], [1865, 63, Meyer and Mendeleev], [1940. 86, -], [1973, 105, -] and [1987, 109, -]. Among the first attempts to classify chemical elements, we may mention the Doebereiner triads, the Pettenkofer groupings, the Chancourtois spiral, the Newlands octaves and the tables by Olding and Lothar Meyer (cf. ref. 1). In particular, the classification into triads (C1. Br. I). (S. Se. Te). (Ca. Sr. Ba). (L1. Na. K) and (Fe. Co. Ni). by Doebereiner (1829), already contains some trends of the periodic table. A great deal of ingredients of the periodic table appear in the classification into spiral by Chancourtois (1862) and in the classification into octaves by Newlands (1864). The Newlands law of octaves (ref. 2), may be summed up by the following arrangement:

H Li Be B C N C

F Na Mg Al Si P S

Cl K Ca Cr Ti Mn Fe

the classification by the French engineer and geologist. Alexandre Beguyer de Chancourtois, the chemical elements are ordered, in increasing atomic weights, on a spiral drawn on a right cylinder, with a periodicity of order 8 (see ref. 3). The latter two classifications already emphasize the notion of periodicity of the chemical (and physical) properties. (For example, all the elements located on a same generatrix of the Chancourtois spiral exhibit similar chemical properties.) A few years after the works by Chancourtois and Newlands. Lothar Meyer and Dmitri Ivanovitch Hendeleev gave to the classification of the elements a more elaborate form. More specifically, the Russian chemist Mendeleev (who worked at Paris in the laboratory of the French physician and chemist Wurtz) set up in 1859 a periodic system of elements groups and rows, where chemically similar elements are placed one under the other (refs. 4-5). Such a sytem comprized ten horizontal (corresponding to 7 periods) and eight vertical columns (corresponding to 8, rather than 9, groups since at that time the group of rare gases was not known).

The periodic table by Mendeleev lies on the periodicity of chemical properties of the 63 elements (over the 92 natural _elements) known at his time. Indeed, Mendeleev found that by disposing elements in increasing atomic weights, the periodicity of their chemical properties is correctly reflected the under condition to make some inversions among the various elements "symbol(atomic number Z, atomic weight)". e.g., I(Z = 53, 126.9) <---> Te(Z = 52, 127.6). (We now know two other inversions, viz., K(Z = 19.39.1) $\langle --- \rangle$ Ar(Z = 18, 39.9) and Ni(Z = 28.58.7) $\langle --- \rangle$ Co(Z = 27, 58.9). Therefore, the notion of atomic number Z

is inherent to the Mendeleev chart: the latter three reflect the fact that Z(Ar) < Z(K) + Z(Co) < Z(Ni) and Z(Te) < Z(1). can be foreseen that the relevant factor characterizing the position of an element in the periodic table is its atomic number rather than its atomic weight.) The work Mendeleev was worthy not only for simple classification and rationalization purposes but also for prediction purposes. matter of fact, in his 1869 table, in order to respect the periodicity of the chemical properties. Hendeleev left some and predicted the existence of some new elements together boxes with their main properties, approximate atomic mass and production particular, he predicted the occurrence, in a column mode. I n between Si(Z = 14) and Sn(Z = 50), of an element (that he called ekasilicium) with approximate atomic mass 72. Such an element was isolated in 1885 by Vinckler and noω called 18 germanium (Ge(Z = 32)).

The atomic number Z is of considerable importance for the periodic table. It determines the chemico-physical properties of the atom. (Such an assertion was published, probably for the first time, by van der Broek in 1913, see ref. 1.) Of course, this number was not specified in the original Mendeleev chart but, as foreseen. the ordering of the chemical elements in the chart reflected the increasing order of Z. (It is to be noted terminology "atomic number" wae used in the Newlande classification. see ref. 1.) The works by Rutherford (1911), on the atomic nucleus, and by Moseley (1912), on X-ray spectroscopy, then showed that the atomic number Z possesses a deep physical property: number Z of a given element is equal, in units of minus the electronic charge, to the charge of the atomic nucleus considered element. Therefore, Z turns out to be the number of electrons in the electronic cloud of the element in its neutral

form. Furthermore, referring to the structure in protons and neutrons (which dates back to Heisenberg (1932)) of the atomic nucleus, the atomic number Z is also equal to the number of protons in the nucleus.

The first three quantitative manifestations of the atomic number Z concern the 1911 Rutherford formula $\sigma \in \mathbb{Z}^2$ for the differential cross section in the scattering of α particles, the 1913-1914 Moseley law $\nu^{1/2} = a(Z-b)$ for the frequency of X-ray lines and the 1913 Bohr(-Balmer) formula $E = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} +$

The periodicity, emphasized by Mendeleev in his table, of the chemical properties of elements corresponds in quantum mechanics. roughly speaking, to a repetition of the electronic structure of outer shells. In this direction, the first interpretation of the periodic system on the basis of the (old) quantum theory was suggested by Niels Bohr. Indeed, he proposed in 1922 a building-up principle for the atom based on a planetary (Bohr-Sommerfeld) model with elliptic orbits and on the filling of each orbit with a maximum of two electrons (ref. 6). (It is remarkable that Bohr's atomic "Aufbau" principle integrates (i) the exclusion principle that will be enounced by Pauli in 1925 (ref. 7) and (ii) the rule. credited to Madelung, that will appear in an explicit form in 1936 (refs. 8-9, see also ref. 10). As a result, Bohr obtained a periodic chart where the transition metals and the rare-earth metals occupy a natural place. (Remember that the rare-earth metals occupy one single box in the conventional periodic table

with 18 columns, cf. for example ref. 11.) This new presentation of the periodic table led Bohr to suggest the existence of a new element with Z=72 and belonging to the family of Ti(Z=22) and Zr(Z=40). Indeed, the element Hf(Z=72) was discovered in Zr minerals a short time later this suggestion and named hafrium after Kobenhavn (see ref. 12). (Hafnium is also known as celtium.)

Since the Bohr pioneer work, the periodic table has received other quantum mechanical explanations. There exits a large number of formats for the periodic system (see for example ref. 11) and now several quantum mechanical (and quasi-quantum there i8 mechanical) approaches of the periodic system of elements (see refs. 12-21). In general, these approaches are based on the Rutherford concept of the atomic nucleus, the atomic shell model (in a Schroedinger, rather than a Bohr, approach), the Pauli exclusion principle and a given rule to fill up the various one-electron quantum levels. In detail, the energy levels of a hydrogen-like atom or the energy levels resulting from self-consistent field calculations define atomic shells nl, n'l', n''l''. ...; the filling of the obtained shells with Z electrons according (i) a given ordering rule and (ii) the Pauli exclusion principle produces a ground electronic configuration which characterizes the chemical element, with atomic number Z, in its neutral form. In the case of atomic shells resulting from self-consistent field calculations, the ordering rule amounts to fill up the shells after their increasing energies. In a somewhat idealized situation, the ordering rule is the so-called Madelung rule (refs. 8-9).

In recent years, the periodic system of chemical elements has also been given a group theoretical articulation (refs. 22-38). Along this vein, a group structure of the periodic system has been discussed by Barut (ref. 22) on the basis of the group SO(4.2) and

extensively investigated by a Russian group (refs. 29-35) on the basis of the direct product group SU(2)xSU(4.2). (The groups SU(2) and SO(4.2) are used in various areas of Physics and Chemistry. For example, the special unitary group in 2 dimensions SU(2) may serve as a spectral group for labelling spin states and the special pseudo-orthogonal group in 4+2 dimensions SO(4.2) as a spectral group for labelling discrete plus zero-energy plus continuous states of a hydrogen-like atom.) More precisely, the work in refs. 32-34 about neutral chemical elements is centered on the use the chain $SU(2) \times SO(4.2) > SU(2) \times SO(4) > SU(2) \times SO(3)$ οf alternatively, $SU(2) \times SO(4,2) > SU(2) \times SO(4) > SU(2) \times SO(3) > SU(2)$ while the work in ref. 22 makes use of the chain of groups SO(4.2) > 50(4.1) > 50(4) for ionized atoms and the chain of groups 50(4.2) $> 50(3.2) > 50(3)\times0(2)$ for neutral atoms.

It is one of the aims of this paper to describe a periodic system for neutral elements based on the group SU(2)xSO(4,2). Indeed, the periodic table to be reported here turns out to be a simple rewriting, with some re-ordering, of the table originating in refs. 29-35 and proposed by Byakov, Kulakov, Rumer and Fet (refs. 32-34). The rest of the present paper is organized as follows. In a second section, we describe the construction of periodic table based on the Madelung rule which arises in the atomic shell model. Then, in a third section, we give the main ingredients for the construction of a periodic table from a chain of groups starting with the group SU(2)xSO(4.2). It is also shown, in the third section, how the latter table is connected to the one of the second section. Finally. an exhaustive (although incomplete) bibliography closes the present paper and shows that the classification of chemical elements is still the object of numerous studies. The bibliography also includes some works concerning the classification of molecules via group theory.

CENTRAL-FIELD MODEL AND PERIODIC SYSTEM

The various shells nl and, more precisely, the various quantum states characterized by the triplets (n.l.m) can be obtained in the central-field model in (at least) two ways.

- (1) One electron is embedded in the (spherically symmetric) Coulomb potential created by a nucleus: we have the familiar hydrogen (or hydrogen-like) atom for which n. 1 and principal quantum number, orbital quantum number and magnetic quantum number. respectively. The one-electron $E - Z^2/(2n^2)$ depends only on n and the degree of degeneracy of E is the Stoner (1924) number n2 (or 2n2 if the spin degeneracy is taken into consideration). The energy E increases with n. a situation we may depict by Ef(n).
- (ii) Each electron of a complex atom is embedded ı n spherically symmetric potential which corresponds to the superposition of the Coulomb field of the nucleus and an average (self-consistent) field created by the other electrons: retain their usual significance while the number in is such that n-1-1 is the number of nodes of the radial wave function associated to the triplet (n,).m). In this case, the one-electron energy E depends on the orbital quantum number 1 and on the number n. Two extreme eituations may occur. First, the energy E increases with n and, for a given value of n, with l, a situation we depict by Second, E increases with n+l and, for a given value of n+1, with n, a situation we depict by Ef(n+1,n).

In both cases (i) and (ii), the spin quantum numbers s=1/2 and $\sigma=\pm k$ for each electron are introduced as further degrees of freedom. We are thus left with quantum states characterized by $(n,1,m,\sigma)$. We may think to produce a table of elements by filling with electrons the various quantum states: the Z electrons of an atom are distributed on the Z quantum states having the lower

energy. (The Pauli exclusion principle is taken into account by associating at most one electron to each quartet $(n,1,m,\sigma)$ or two electrons to each triplet (n,1,m).) The rule Ef(n) cannot be used for the building-up of the neutral atom. The rule Ef(n,1) may be used to construct the chemical elements in their neutral form from Z = 1 to Z = 18 but breaks down for the first time when Z = 19. The latter fact was recognized by Bohr (ref. 6) who replaced Ef(n,1) by the rule Ef(n+1,n). The rule Ef(n+1,n) is referred to as Madelung rule (see ref. 9). Goudsmit rule or Bose rule (see ref. 12).

The Madelung rule, which has been re-discovered on various occasions, has received much attention. In particular, it is well known that the statistical and semiclassical Thomas-Fermi model of the neutral atom can be used to approximately account for the first part of the Madelung rule (see, for instance, refs. 10 and 20). Further, the first part of the rule Ef(n+1,n) has been recently investigated from an exactly soluble eigenvalue problem (ref. 15) and from a group theoretical approach (refs. 23-24).

As a net result, the Madelung rule leads to the following order for the increasing one-electron energies:

Electron	states	Total	degeneracy
(ls)			2
(2s, 2p)			8
(3e. 3p)			8
(4s, 3d,	4p)		18
(58, 4d.	5p)		18
(6s, 4f,	5d, 6p)		32
(7s, 5f,	6d, 7p)		32
• • •			

where the levels in () are also ordered after increasing energies.

Note that the total degeneracy of the levels in () reflects the

variation ΔZ , of the atomic number Z, corresponding to two consecutive rare gases: $\Delta Z(\text{He}\rightarrow\text{Ne}) = \Delta Z(\text{Ne}\rightarrow\text{Ar}) = 8$, $\Delta Z(\text{Ar}\rightarrow\text{Kr}) = \Delta Z(\text{Kr}\rightarrow\text{Xe}) = 18$, $\Delta Z(\text{Xe}\rightarrow\text{Rn}) = \Delta Z(\text{Rn}\rightarrow\text{118}) = 32$, ... (cf. ref. 12).

We may then construct a periodic table from the Madelung rule in the following way. Let us consider the skeleton

0 1 2 3 5 1 [1 1] 2 [2 2] [3 2] 3 [3 3] [4 3] [5 3] [4 4] [5 4] 4 [6 4] [7 4] [5 5] [6 5] 5 [7 5] (8 5) (9.5)6 [6 6] . . .

where the rows are labelled with $n = 1, 2, \ldots$ and the columns with $l = 0, 1, \ldots$ and where the entry in the n-th row and the l-th column is [n+1, n]. This provides us with the skeleton of a (periodic) table where the various blocks [n+1, n] are filled in the "n+1 n" dictionnary order with chemical elements of increasing atomic numbers, the block [n+1, n] containing 2(2l+1) elements. As a result, we obtain the table (where each element is denoted by its atomic number 2):

1 2] 3 4] 5 6 .. 101 [[11 12] [13 14 .. 18] [21 22 .. 30 1 [19 20] [31 32 .. 36] [39 40 .. 48] [57 58 .. 70] [37 38 1 [49 50 .. 54] [71 72 .. 801 [89 90 .. 102] [.. [55 56] [81 82 .. 86] [103 104 .. 112] [139 140 .. 152] [.. [87 88] [113 114 .. 118] [153 154 .. 162] [.. [119 120] [163 164 .. 168] [.. [169 170] ι..

[..

7

GROUP THEORY AND PERIODIC SYSTEM

In addition to the point symmetry group SO(3), other Lie groups are of interest for the hydrogen atom problem. It is well known that the dynamical invariance groups are SO(4) for the discrete spectrum and SO(3,1) for the continuous spectrum. Further, a noninvariance dynamical group which accounts for the discrete plus zero energy plus continuum states is SO(4,2), a noncompact Lie group having 15 generators (see refs. 39~42). This group was obtained in refs. 40-42 by an ascent process from O(4,1) to O(4,2). Another derivation of the group SO(4,2) for the hydrogen(-like) atom spectrum has been obtained recently by a descent process from Sp(8,R) to SO(4,2) (refs. 43-48). (The real symplectic group in 8 dimensions Sp(8,R) is a noncompact Lie group with 36 generators.)

From a practical point of view, there is a representation of SO(4,2) that contains all states of the hydrogen atom: the set of all states of the hydrogen atom can be regarded as an infinite multiplet of the group SO(4,2). This is the starting point for the construction of a periodic chart based on a group theoretical approach. In such an approach, the chemical elements are treated as structureless particles and considered as states of a system controlled by a given group. For evident reasons, the group SO(4,2) is a guite natural candidate.

The relevant infinite multiplet of SO(4,2) can be organized multiplets of SO(4) and SO(3). The multiplets of SO(4) may be disposed into rows characterized by the IRC (irreducible representations class) labels $\nu = 1, 2, 3, \ldots$ The vth row contains ν multiplets of SO(3) characterized by the IRC labels $\lambda = 0, 1, 2, ..., \nu-1.$ This leads to a frame, with rows labelled by ν and columns by λ , in which we put a block $[\nu+\lambda \ \nu]$ at the $\nu-\lambda$ entry, in complete analogy with the skeleton described in the second section. The block $[\nu+\lambda \ \nu]$ contains $2\nu+1$ sub-blocks and

each sub-block can be divided into two boxes so that the considered block contains $2(2\nu+1)$ boxes: the resulting doubling may be accounted for by the introduction of a group SU(2): we thus pass from SO(4,2) > SO(4) > SO(3) to $SU(2) \times SO(4,2) > SU(2) \times SO(4) > SU(2) \times SO(4) > SU(2) \times SO(3) > SU(2) \times SO(4) > SU(2) \times SO(3) > SU(2)$. The boxes in the block $[\nu+\lambda \ \nu]$ are organized in multiplets of the queue group SU(2): $[\nu+\lambda \ \nu] = [\Re(\iota \times)]$ where $\iota = abs(\lambda-b)$, $abs(\lambda+b)$ and $x = -\iota$, $-\iota+1$, ..., ι . Thus, the block $[\nu+\lambda \ \nu]$ contains two multiplets of SU(2) for $\lambda \neq 0$ and only one for $\lambda = 0$. As a final step, each box in the block $[\nu+\lambda \ \nu]$ is characterized by an address $(\nu\lambda\iota \times)$ with ι and, for fixed ι , \times increasing from left to right.

Contact with chemistry is as follows. The box $(\nu\lambda\iota x)$ is filled with a chemical element the atomic number Z of which is given by (cf. refs. 22 and 34)

 $Z=d(d^2-1)/6+(d+1)^2/2-a(d+1)/2-4\lambda(\lambda+1)+\lambda+\iota(2\lambda+1)+x-1$ where $d=\nu+\lambda$, a=1(0) for d even(odd). We shall refer the chart so-obtained to as Table M. It is remarkable that Table M is very close to the one of the second section. The only difference is that in Table M the elements in a given block $\{\nu+\lambda,\nu\}$ are arranged in one or two multiplets of SU(2) according to as $\lambda=0$ or $\lambda\neq0$.

Table M resembles to some extent other periodic tables. particular Table M is, up to the exchange of rows and columns, identical to the table introduced by Byakov, Kulakov, Rumer and Fet The presentation adopted here leads to a table the (refs. 32-34). format of which is easily comparable to the one of most of existing tables. Furthermore Table M exhibits. up to a rearrangement, the same blocks as the table by Neubert (ref. 14) based on the filling of only four Coulomb shells. Finally, Table M (and therefore the tables of refs. 32-34 and ref. 14) presents, rearrangement, some similarities with the table by Dash (ref. 13) based on the principal quantum number, the law of second

order constant energy differences and the Coulomb-momentum interaction, except that in the latter table the third transition group does not begin with Lu(Z=71), the lanthanide series does not run from La(Z=57) to Yb(Z=70) and the actinide series does not run from Ac(Z=89) to No(Z=102).

The main specificities of Table M may be seen to be the (i) hydrogen is in the family of alkali metals, (ii) following: helium belongs to the family of alkaline earth metals and (iii) the inner transition series (lanthanides and actinides) as well as the transition series (iron group, palladium group and platinum group) occupy a natural place. This is to be contrasted with the conventional tables in 8(9) or 18 columns where (i) hydrogen is sometimes located in the family of halogens, (11) helium generally belongs to the family of noble gases and (111) the lanthanide Beri**e**B and the actinide series are generally treated like appendages. Following the discussion in ref. 34. the distribution Table M of the elements with 104 ≤ Z ≤ 120 is in agreement with the predictions by Seaborg (see ref. 17) based on atomic shell model calculations. In contrast to his predictions, however, Table M shows that the elements with 121 5 Z 5 132 form a new family having no homologue among the known elements. Further, Table M suggests that the family of superactinides contains the elements with 139 ≤ Z ≤ 152 (and not with 122 ≤ Z ≤ 153 as predicted by Seaborg).

The chemist is interested in atoms and ions but also in There exists various attempts to construct periodic tables for molecules (see refs. 49-52 and references therein). close this section, some comments about the implications for molecular systems of the table for chemical elements described in present paper are in order. From a group theoretical viewpoint, a periodic table for neutral elements or, in a certain sense, for 1-atom molecules can be used in a recurrent way to produce a periodic table for N-atom molecules. For example, by starting with the periodic table for chemical elements based on the group $G(1) = SU(2) \times SO(4,2)$, one may construct a periodic table diatomic molecules from the consideration of the Kronecker product $G(2) = G(1) \times G(1)$ (ref. 50). More generally, a periodic system

N-atom molecules can be set up from the study of a chain of groups starting with the head group $G(N) = G(1) \times G(1) \times \dots \times G(1)$. (In a very genera) approach, the N factors in G(N) are not necessarily all identical.)

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