wartende Regelmäßigkeit, gemäß der bei diesen Komplexen die Streckschwingungskraftkonstanten der Technetiumhalogenbindungen sich immer kleiner als die der entsprechenden Rheniumhalogenbindungen erweisen.

Herrn Prof. Dr. K. H. HANSEN, Universität Bonn, möchten wir für viele wertvolle Hinweise verbindlich danken. Herrn Prof. Dr. W. HERR, Universität Köln, und Herrn Priv.-Doz. Dr. H. W. NÜRNBERG, Zentrallabor für Chemische Analyse der KFA Jülich GmbH, danken wir für die freundliche Förderung dieser Arbeit.

Double Shell Structure of the Periodic System of the Elements *

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A new periodic system of the elements (PSE) is proposed which exhibits symmetry properties not apparent in the conventional arrangement of the elements. By discussing the solutions of the non-relativistic Schrödinger equation for the Coulomb problem it is shown that the PSE might be based on the filling of only four Coulomb shells as compared to the partial filling of up to eight shells in the conventional classification. On the other hand, the multiplicity of the states in the PSE appears to be four as compared to two due to spin in the hydrogen spectrum. A transformation of the PSE-spectrum into the hydrogen spectrum is possible by a rotation in quantum number space.

1. Introduction

The Periodic System of the Elements (PSE) reflects the order of filling of the electron shells and subshells. It is a generally accepted rule that this order is *in principle* identical with the sequence of the electronic states in the hydrogen atom. The well known exceptions from the expected order of filling occuring in the PSE are ascribed to the modification of the unscreened Coulomb field due to the presence of other shell electrons and to the interactions among these electrons and have been justified by detailed calculations of the energies involved.

However, the exceptions from the rule in the second half of the PSE are so numerous that one might well ask: Is the sequence of the hydrogen states really the underlying principle in the build up of the PSE or is it possible to find a more adequate principle?

In persueing this question, we concentrate on the major exceptions where complete subshells are filled against the rule, e. g. the filling of the 4s subshell before the 3d subshell. We shall neglect the minor irregularities occuring within some of the subshells; especially, with respect to the beginning of the lantanides, La is taken to be the first element with an electron in the 4f subshell, since here the intermediate occupancy of a 5d state can be considered as a minor exception similar to that occuring in the case of Gd at the center of the lantanides.

It is evident that the problem of finding a simple build up principle implies a rearrangement of the conventional PSE.

After a suitable system is presented in Sect. 2, the dependence of some properties of the elements on their position in the new PSE will be discussed in Sect. 3. In Sect. 4 the solutions of the Schrödinger equation for a Coulomb potential will be discussed and it will be shown that both the PSE-spectrum and the hydrogen spectrum are solutions of the Coulomb problem. The spectra transform into each other by a rotation in quantum number space.

2. Formal Description of the New PSE

The new PSE is shown in Fig. 1. It is obtained by first turning the conventional system up side down in order to obtain the correlation between energy and quantum numbers in a customary way. Then the group I and group II elements are pulled one unit down and written to the right of the other elements.

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[1] E. MADELUNG, Die mathematischen Hilfsmittel des Physikers, Springer-Verlag, Berlin 1950, p. 611. See footnote p. 670 in [2] for the early reference in 1926.

[2] S. A. GOUDSMIT and P. I. RICHARDS, Proc. Nat. Acad. Sci. US **51**, 664 [1964].

$\ell=3$														$\ell=2$										$\ell=1$						$\ell=0$		$\bar{N}$	N
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw	104 Ku	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	3	8
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	87 Fr	88 Ra		7
														39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	55 Cs	56 Ba	2	6
														21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	37 Rb	38 Sr		5
																								13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	19 K	20 Ca	1	4
																								5 B	6 C	7 N	8 O	9 F	10 Ne	11 Na	12 Mg		3
																														3 Li	4 Be	0	2
																														1 H	2 He		1

Fig. 1. The Periodic System of the Elements (PSE). For the shell number holds: $N=n+l$, $\bar{N}=\hat{l}=l_{\max}$ of the shell.

A classification in terms of the conventional principal quantum number n and the orbital quantum number l is given in Fig. 2. Evidently, for each single shell not n is a constant but $N=n+l$. This possibility of characterization has been noticed as early as 1926 by MADELUNG[1] and has again been stressed only recently by GOUDSMIT and RICHARDS[2]; however, no further conclusions were drawn.

8-SHELL-CLASSIFICATION

n, ℓ				N
5f	6d	7p	8s	8
4f	5d	6p	7s	7
	4d	5p	6s	6
	3d	4p	5s	5
		3p	4s	4
		2p	3s	3
			2s	2
			1s	1

$N = n + \ell$

Fig. 2. 8-Shell-Classification of the PSE in terms of the conventional quantum numbers.

In fact, as evident from Fig. 1, the PSE exhibits high symmetry. It consists of boxes which form a triangular matrix. Each box contains $4(2l+1)$ elements. The multiplicity $(2l+1)$ is due to the well known space degeneracy as described by the magnetic quantum number m with the values

$$-l \leqq m \leqq +l .$$

There is a doubling of states in the horizontal direction which is ascribed to the spin s, $s=\pm 1/2$ and a similar doubling in the vertical direction which we shall describe analogous to the spin by introducing tentatively a new quantum number c, $c=\pm 1/2$.

Clearly, the PSE exhibits a *double shell* structure in a *twofold sense:* a) There is a shell structure both in the horizontal and vertical direction and b) each shell is at least a double shell.

3. Properties of the Elements

From the chemist's point of view, the new PSE preserves at large the relative position of the usual chemical groups. In addition, proceeding along the outer edges either horizontally or vertically, there is in general only a relatively small change in the chemical properties of the elements; if this rule could be put on a physical basis, the chemical similarity of the lantanides would need no special justification. As a byproduct, in the new PSE alkali halides are centered naturally around the noble gases in a similar way as the III – V and II – VI semiconductors are centered around the elemental ones.

It is an essential feature of the conventional PSE that it exhibits a shell structure in the *horizontal direction.* Many physical and chemical properties vary more or less continuous with increasing filling of the $2(2l+1)$ states in a given subshell l, but there is a discontinuous change in going horizontally from one subshell to the next. If the notion of double shells in the *vertical direction* is of physical reality, one should expect a discontinuous behaviour by proceeding along the elements of a given chemical group.

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[3] HÜTTE, Taschenbuch der Werkstoffkunde (Stoffhütte), Akademischer Verein Hütte, Hrsgb., Berlin 1967, p. 18.

In Fig. 3 the electronegativity[3] of the elements is plotted for each chemical group as a function of $N = n + l$. The elements with odd N belong to the lower halves of the double shells and are represented by black symbols, the elements with even N are in the upper halves and are represented by open symbols. Two consecutive elements of the same group are connected by a full line if they belong to the same double shell, and by a dotted line if they belong to different ones.

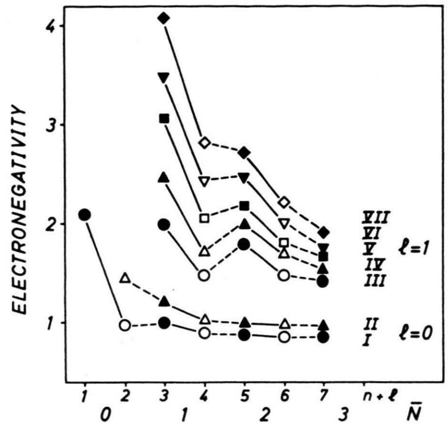

Fig. 3. Double shell structure in the electronegativity along the chemical groups.

The double shell structure is very pronounced in the group III elements (B, Al, Ga, ...). Clearly, the slope of the first dotted line is here opposite to the slope of the full lines. However, due to the strong background variation, the opposite slopes of full and dotted lines are in many cases suppressed; this fact should not give rise to the impression that two elements of different double shells are *basically* more similar than two of the same double shell.

Similar curves may be obtained for other properties which depend on the outer electrons. As a rather basic property the ionization energies[4] are shown in Fig. 4. Opposite slopes are barely indicated, but the different general appearance of the full lines compared to the dotted lines is in accordance with the assumption of double shells in the vertical direction. One can show by appropriate plots that with increasing nuclear charge of isoelectronic atoms the double shell structure in the ionization energies for the last electron becomes less pronounced in accordance with the observation that highly ionized atoms obey[2] the hydrogen level spectrum, which, of course, does not have a vertical structure.

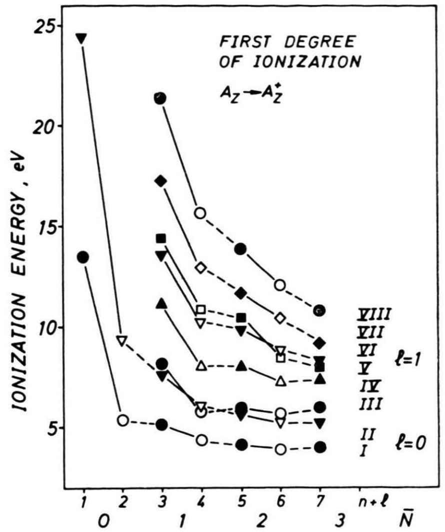

Fig. 4. Double shell structure in the ionization-energies along the chemical groups.

4. Theoretical Interpretation

4.1. Solutions of the Schrödinger equation

In solving the Schrödinger equation for a Coulomb potential, there is some freedom in the choice of a certain constant $\varkappa$. This fact is well known[5], but in the past only that value of $\varkappa$ which leads to the spectrum of the H-atom has been considered to be of significance. In the following the Coulomb problem shall be reconsidered by paying special attention to the role of $\varkappa$ with respect to the generation of different spectra.

In spherical coordinates, the radial part of the wave equation is given[5] by:

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)-\frac{Ze^2}{r}R+\frac{l(l+1)\,\hbar^2}{2\mu r^2}R=E\,R\,. \tag{1}$$

We consider only bound states, i. e. the energy is assumed to be negativ, $E = -|E|$. We define the dimensionless quantities ϱ, $\varkappa$, λ by

$$\varrho = k\,r/\varkappa\,, \tag{2 a}$$

$$1 = 2\,\mu\,|E|/\hbar^2 k^2, \tag{2 b}$$

$$\lambda = \varkappa\,2\,\mu\,Z\,e^2/\hbar^2\,k \tag{2 c}$$

and obtain Eq. (1) in the dimensionless form

$$\frac{\mathrm{d}}{\mathrm{d}\varrho}\left(\varrho^2\frac{\mathrm{d}R}{\mathrm{d}\varrho}\right)-\left[l(l+1)-\lambda\,\varrho+\varkappa^2\,\varrho^2\right]R=0\,. \tag{3}$$

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[4] Lit. [3], p. 20.

[5] L. SCHIFF, Quantummechanics, McGraw-Hill 1955, p. 82.

Assuming a solution of the form

$$R(\varrho) = \varrho^l\,[a_0 + a_1\,\varrho + a_2\,\varrho^2 \ldots]\, e^{-\varkappa\varrho} \tag{4}$$

results, by ordering in power of ϱ, in

$$\sum_{\nu=0} \varrho^\nu [\,(\nu+1)\,(\nu+2\,l+2)\;a_{\nu+1} + (\lambda - 2\,\varkappa(l+1) - 2\,\varkappa\,\nu)\;a_\nu] = 0\,. \tag{5}$$

The usual termination condition on the polynomial $\Sigma\; a_\nu\,\varrho^\nu$ at a finite ν, say $\nu = n_\mathrm{r}$, gives the condition for the alowed values λ,

$$\lambda = 2\,\varkappa(n_\mathrm{r} + l + 1) = N^* \tag{6}$$

where the choice of $\varkappa$ is still arbitrary. Any $\varkappa > 0$ ensures the quadratic integrability of $R(\varrho)$.

Equation (2b) suggests, that k may be identified with a wave number which by Eq. (2 a) is confined to the values

$$k_{n^*} = \varkappa\,k_0/\lambda = k_0/n^*, \quad k_0 = 2\,\mu\,Z\,e^2/\hbar \tag{7}$$

which are with

$$\lambda/\varkappa = n^* = 2\,(n_\mathrm{r} + l + 1) = 2, 4, 6, \ldots \tag{8}$$

independent of $\varkappa$. From Eqs. (7) and (2 b) the allowed energies

$$E_{n^*} = -\,|\,E_{n^*}| = -\,E_0/n^{*2}, \quad E_0 = 2\,\mu\,Z^2\,e^4/\hbar^2 \tag{9}$$

are thus independent of $\varkappa$ also.

The sequence of energies E_{n^*}

$$E_2 = -\,E_0/4, \quad E_4 = -\,E_0/16, \quad E_6 = -\,E_0/36, \ldots \tag{10}$$

is a universal property of the Coulomb potential and is, therefore, apart from the different labelling, in particular identical to that of the H-atom. In the conventional treatment of the H-atom, however, one introduces a principal quantum number n,

$$n = n^*/2 \tag{11}$$

and then labels the energies by n, $E_n = -\,E_0/4\,n^2$ with $n = 1, 2, 3, \ldots$. It appears that n has to be considered a short notation for $n^*/2$.

Since the energies are independent on $\varkappa$, they cannot be used for distinguishing spectra with respect to different $\varkappa$. However, because of Eq. (6) a suitable classification is possible in terms of the quantum number $\lambda(\varkappa)$.

4.2. *Classes of Spectra*

Let us consider the two cases $\varkappa = 1/2$ and $\varkappa = 1$. The first case corresponds to the generation of the hydrogen spectrum, the second will turn out to correspond to the generation of the PSE-spectrum.

From Eq. (6) we have for $\varkappa = 1/2$:

$$\lambda = (n_\mathrm{r} + l + 1) = N^*, \quad N^* = 1, 2, 3, \ldots\,. \tag{12}$$

By Eqs. (8) and (11) holds, rather incidentically, $N^* = n$. Therefore, the conventional classification of the hydrogen states in terms of n conceals the significance of $\varkappa$ in the generation of the spectrum.

In case of the PSE however, the rôle of $\varkappa$ seems to be of some importance. From Eq. (6) we have for $\varkappa = 1$:

$$\lambda = 2\,(\bar n_\mathrm{r} + l + 1) = N^*, \quad N^* = 2, 4, 6, \ldots \tag{13a}$$

where the bar-notation is used simply for the purpose of differentiation from the case $\varkappa = 1/2$. Since l and $\bar n_\mathrm{r}$ are by Eq. (4) integer numbers, N^* can indeed assume only even numbers.

Each of the states with $N^* = \text{const}$ carries a contribution of twice the angular momentum quantum number l and this is exactly the property which is characteristic for the PSE. However, in the conventional classification of Fig. 2 the principal quantum number $n = n_\mathrm{r} + l + 1$ is used and Eq. (13 a) reads

$$\lambda = n + l + 1 = n_\mathrm{r} + 2\,l + 2 = N + 1. \tag{13b}$$

By comparison of Eqs. (13 a) and (13 b) one obtains

$$n_\mathrm{r} = 2\,\bar n_\mathrm{r}\,, \qquad N + 1 = N^*. \tag{14, 15}$$

The relationship (14) has to be considered as the definition of a short notation for $2\,\bar n_\mathrm{r}$ and hence n_r must be even. Similarly, by Eq. (15), $N+1$ can assume only even values corresponding to the allowed values of N^* given in Eq. (13 a). Apparently, the classification of the PSE given in Fig. 2 contradicts in part these conditions. In fact, only every second shell of Fig. 2 survives if these conditions are imposed and one obtains the spectrum given in Fig. 5 a which may be written in terms of $\bar n_\mathrm{r}$ and l as given in Fig. 5 b.

4 - SHELL-CLASSIFICATIONS

n,l				$\bar N^*$	$\bar n_r,l$				$\bar N$	$\bar n,l$			
4f	5d	6p	7s	8	0,3	1,2	2,1	3,0	3	4f	4d	4p	4s
	3d	4p	5s	6		0,2	1,1	2,0	2		3d	3p	3s
		2p	3s	4			0,1	1,0	1			2p	2s
			1s	2				0,0	0				1s

Fig. 5. 4-Shell-Classification of the PSE in terms of (from left to right) a) the conventional quantum numbers n and l; b) the PSE-quantum numbers $\bar n_\mathrm{r}$ and l; c) the PSE-quantum-numbers $\bar n = \bar n_\mathrm{r} + l + 1$ and l.

Since the number of elements in the PSE is a physical reality and beyond discussion, by comparison of Fig. 5 with Fig. 1 we conclude that in fact pairs of rows rather than single rows (as in the case of the H-atom) form complete shells and that the degeneracy of a PSE-shell is twice that of a hydrogen shell. In order to lift this additional degeneracy, analogue to the postulation of a spin $s = \pm 1/2$ in the non relativistic treatment of the hydrogen atom, we postulate for the PSE in addition a quasi spin property described by a quantum number $c = \pm 1/2$. Similar to the total angular momentum quantum number $j = l + s = l \pm 1/2$ a total radial quantum number q may be defined as

$$q = \bar{n}_r + c = \bar{n}_r \pm 1/2 = q_\pm ,$$

where the states q_+ correspond to the upper and the states q_- to the lower half of a double shell.

Every element of the PSE is thus defined by a set of five quantum numbers $(\bar{n}_r, c; l, m, s)$. The boxes of the PSE (Fig. 1) are obtained by generating the set (Fig. 5 b):

$$\{(\bar{n}_r, l)\} = \{(\nu, \overline{N} - \nu)\}_{\overline{N} = 0, 1, 2, \ldots, d (= 3)}^{\nu = 0, 1, 2, \ldots, \overline{N},} \tag{16 a}$$

where $\overline{N}$ is used as a short notation for $(N-2)/2$. The multiplicity $4(2l+1)$ of each box, produced by

$$c = \pm 1/2, \quad -l \leqq m \leqq +l, \quad s = \pm 1/2 \tag{16b}$$

gives then the $4(2l+1)$ chemical elements of the box.

If we define a principal quantum number $\bar{n}$ such that it is of the same form as the conventional principal quantum number n,

$$\bar{n} = \bar{n}_r + l + 1 \tag{17}$$

the states $(\bar{n}, l)$ of a double shell in the PSE look the same as the states of a shell in the H-atom (Fig. 5 c). The order of filling, however, is opposite in the two cases.

It may be mentioned that a substitution $2l = \bar{l}$ which would reduce Eq. (13 b) to the form of Eq. (12), is not possible since the degeneracy of a state $\bar{l}$ would be different from $2(2l+1)$ as required by a row of the PSE. Physically, l is uniquely defined by the rotational symmetry of the problem and cannot be reinterpreted.

With respect to the nomenclature it would be of some advantage not to introduce a principal quantum number at all, but rather use the maximum angular momentum $\hat{l}$ of the shell instead. If one designates further the radial quantum number not by n_r but by l', one has simply for every shell

$$l + l' = \hat{l} = \text{const}.$$

The energies depend on $(\hat{l}+1)$ and for $\hat{l} = 0$ one has a zero point energy as in the case of the harmonic oscillator.

4.3. *Wave Functions*

The coefficients in the dimensionless radial wave functions, Eq. (4), depend on $\varkappa$ as given in Table 1; in physical space, however, the radial functions are independent on $\varkappa$ and can be written as

$$R_{\varkappa, n^*, l}(r) = A_0 \, e^{-k_0 r/n^*} \left(\frac{k_0 r}{\varkappa n^*}\right)^l L^{2l+1}_{\frac{1}{2}n^*+1} \left(\frac{2 k_0 r}{n^*}\right) \tag{18}$$

where A_0 is a normalization factor, $L^{2l+1}_{\frac{1}{2}n^*+1}$ are associated Laguerre polynomials, $k_0 = 2 \mu Z e^2/\hbar^2$ and n^* assumes by Eq. (8) only even integers, $n^* = 2, 4, 6, \ldots$. Since the factor $\varkappa^{-l}$ can be absorbed into the normalization constant, the radial functions are – apart from their different labelling – identical to those given in the literature [5] for the hydrogen atom.

The complete wave function for the Coulomb problem should allow for the duplicity of the shells

$\varkappa$	$l=3$	$l=2$	$l=1$	$l=0$	$\hat{l}$
1	1, 0, 0, 0	1, −1/3, 0, 0	1, −1, 1/5, 0	1, −3, 2, −1/3	3
		1, 0, 0, 0	1, −1/2, 0, 0	1, −2, 2/3, 0	2
			1, 0, 0, 0	1, −1, 0, 0	1
				1, 0, 0, 0	0
1/2	1, 0, 0, 0	1, −1/6, 0, 0	1, −1/2, 1/20, 0	1, −3/2, 1/2, −1/24	3
		1, 0, 0, 0	1, −1/4, 0, 0	1, −1, 1/6, 0	2
			1, 0, 0, 0	1, −1/2, 0, 0	1
				1, 0, 0, 0	0

Table 1. The coefficients a_0, a_1, a_2, a_3 of the dimensionless radial functions, Eq. (4), for $\varkappa = 1$ and $\varkappa = 1/2$.

in case of $\varkappa = 1$. The wave function might be written as

$$u^{c,m,s}_{\varkappa,n^*,l} = A\, R_{n^*,l}(r)\; Y_l^m(\vartheta,\varphi)\; \chi_s(\pm 1/2)\; \Gamma_c[\pm(\varkappa - 1/2)] \tag{19}$$

where A is a normalization factor, Y_l^m are spherical harmonics, χ_s and Γ_c are spin and quasi spin functions where the latter reduces to a constant in the case $\varkappa = 1/2$. The well known spin function requires the inclusion of relativistic effects; the physical basis for Γ_c has still to be found.

4.4. Transformation of Spectra

It is known that highly ionized[2] atoms form a periodic system which coresponds to the hydrogen spectrum. This implies that there should exist a transformation which transforms the PSE-spectrum gradually into the hydrogen spectrum if the strength of the Coulomb potential is changed while the number of electrons is kept constant.

We consider a triangular quantum number lattice with a fixed direction being the direction of increasing λ (Fig. 6). Both the hydrogen spectrum and the PSE-spectrum occupy certain lattice points in this lattice. It is evident from Fig. 6 that the required transformation is a rotation of the spectra in the fixed lattice space by an angle δ which is related to the parameter $\varkappa$ of the Schrödinger equation treatment by

$$\cos\delta = \varkappa\,. \tag{20}$$

For $\delta = 0$ we have the PSE spectrum with $\varkappa = 1$ and $\lambda(1) = 2, 4, 6, \ldots$; for $\delta = \pi/3$ we have the hydrogen spectrum with $\varkappa = 1/2$ and $\lambda(1/2) = 1, 2, 3, \ldots$. The discussion of the additional four characteristic angles produced by the sixfold symmetry of the lattice shall be omitted here.

Physically, $\varkappa$ might be interpreted as a measure for the effective potential in the following sense. We write Eq. (2 c) in the form $\lambda = 2\,\mu\, Z^*\, e^2/\hbar^2 k$ with

$$Z^* = \varkappa Z\,. \tag{21}$$

If Z is the nuclear charge, then Z^* is the effective nuclear charge which shall be defined to be equal to the number of electrons which can be bound by the potential. For $\varkappa = 1$, the number of bound electrons is equal to the nuclear charge as it is the case in the PSE. If $\varkappa = 1/2$, the number of bound electrons is equal to half the nuclear charge. In order to get from the atoms of the PSE a periodic system which corresponds to the hydrogen spectrum, for each constant number of electrons in the shell one should by this interpretation increase the nuclear charge by a factor two. – In fact, the binding power per unit nuclear charge is much weaker in case of the hydrogen spectrum than in case of the PSE. It may be reasoned by very general arguments that therefore the hydrogen spectrum is not realized as a periodic system under normal conditions on earth but only in highly excited plasmas.

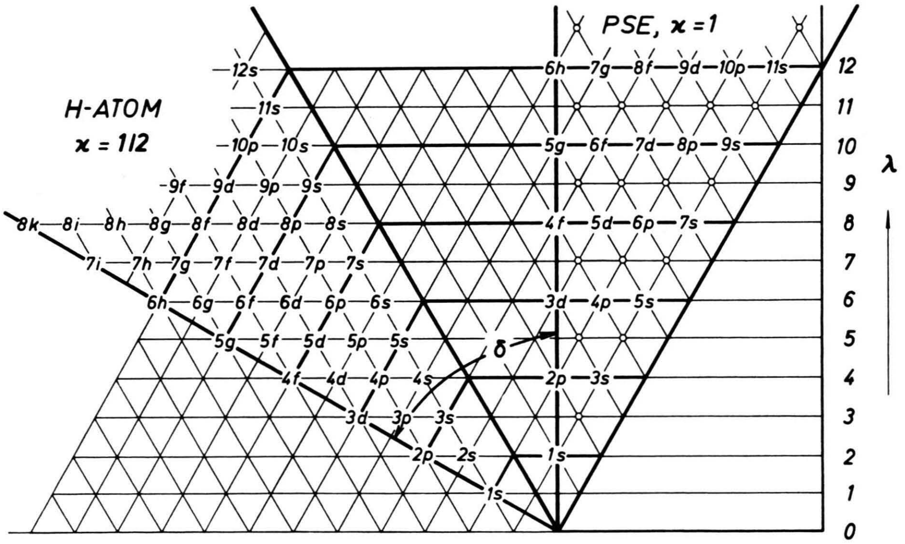

Fig. 6. PSE- and hydrogen-spectrum embedded in a triangular quantum number lattice in the conventional classification. For the PSE, the correct classification may be obtained by using Fig. 5.

The interpretation of $\varkappa$ as a transformation parameter according to Eq. (20) allows some additional information on $\varkappa$ which is not readily obtained from the Schrödinger equation:

a) In Sect. 4.2 we introduced the quasi spin quantum number c in order to generate the actual PSE. As seen from Fig. 6, by rotating the hydrogen spectrum onto the PSE spectrum, certain states (indicated by open dots in the figure) become forbidden. However, if one postulates that no states are to be lost by the transformation, then one is forced to infer the existence of an additional level splitting effect such that the total number of allowed states remains constant.

b) From the Schrödinger treatment the only condition on $\varkappa$ is $\varkappa > 0$. If Eq. (20) is assumed to be indeed correct, than the allowed range for $\varkappa$ is $0 < \varkappa \leqq 1$. Still, neither by Eq. (6) need $\lambda(\varkappa)$ to be an integer in order to define a solution of the Schrödinger Eq. (3) nor is δ by Fig. 6 necessarily confined to special angles. However, from Fig. 6 it is clear that for intermediate angles $\pi/3 > \delta > 0$ the spectra do not coincide with lattice points and one has no pure states. If one considers only pure states, then λ assumes indeed only integer or even integer numbers.

c) The order of filling of the states is obtained from Fig. 6 by assuming a small perturbation which tilts the spectra by an infinitesimal angle. If the hydrogen spectrum is tilted just a bit toward the PSE-spectrum, the order of filling according to increasing λ is correctly inferred as $(n, l) =$ 1s; 2s, 2p; 3s, 3p, 3d;... . Tilting the PSE-spectrum a bit towards the hydrogen spectrum, the order of filling is correctly deduced to be $(\bar{n}, l) =$ 1s; 2p, 2s; 3d, 3p, 3s; 4f, ...

5. Final Remarks

By using the existence of a freely adjustable parameter $\varkappa$ in the simple non relativistic Schrödinger equation for the Coulomb problem, we interpreted the occurance of only double weighted angular momentum quantum numbers in the conventional classification of the PSE (Fig. 1) as being due to a special choice of $\varkappa$. It seems that the most degenerate representation of the PSE requires the filling of only four Coulomb shells with a fourfold degeneracy of the states as compared with the twofold degeneracy due to spin in the conventional classification of the hydrogen spectrum. In the frame of the present simple theory, $\varkappa$ appears to be a rather formal parameter. The fact that this parameter proves to be useful in describing the transformation between the PSE and the hydrogen spectrum suggests, that a more fundamental interpretation should be possible within the scope of a more general treatment of the Coulomb problem. Similarly, the existence of an additional level splitting effect requires a more detailed theory for its explanation then used in this communication. It has been shown recently[6] that the H-atoms can be described by the dynamical group 0(4,2) in a 6-dimensional space. This group is the product $0(4,2) = 0(2,1) \times 0(2,1)$ of two independent Lorentz groups and the effect of spin in one of them should require by reason of symmetry the same in the other; the fourfold degeneracy of the states in the PSE appears then to be quite natural.

The high symmetry of the PSE seems to be of interest from different point of views and further questions arise immediately as may be indicated by the following remarks.

1. Starting from a PSE with only four Coulomb shells, detailed calculations in atomic and solid physics require a quite unusual first order approximation since in contrast to current theories the states with high orbital angular momenta in a shell have – similar to the nuclear states – a lower energy than those with low orbital angular momenta. Further, the tetrahedral bond which is very characteristic for many systems, might perhaps find a more direct interpretation than in terms of an sp^3 hybrid bond.

2. Taking the isotopic spin into account, the nucleus is described basically by five quantum numbers. One expects these quantum numbers to match somehow the five quantum numbers of the electron shell if the total wave function of a complete atom consisting of nucleus and shell is considered. What are then the properties of nuclei corresponding to the atomic magic numbers $Z = 4$, 20, 56, 120? Since for the nucleus a harmonic oscillator potential is a reasonable approximation, it is interesting to note that the total number of states of a three dimensional harmonic oscillator is for every second shell identical to an atomic magic number. Unfortunately, this

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[6] A. O. Barut and H. Kleinert, Phys. Rev. **161**, 1464 [1967]. — Y. Ne'eman, Algebraic Theory of Particle Physics, Benjamin 1967.

is not true anymore if the multiplicity of the states due to spin and isospin is taken into account.

3. By straightforward extrapolation of the PSE one obtains for the far transactinides a new electron shell which has a maximum angular momentum $\hat{l}=4$ and is started with the element $Z=121$.

4. Modern algebraic approach to elementary particle physics has brought out some parallels between the properties of hadrons and the H-atom. It has been shown[6] that not only the H-atom but also the hadron spectrum can be described by the group $0(4,2)$. It seems to be of interest to use the transformation from the hydrogen spectrum to the PSE-spectrum as an experimentally well accessible model for similar problems in the physics of strong interaction. In this connection it would be desirable to obtain more experimental values on the properties of highly ionized atoms than are currently available.

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Vibrational Potential Energy Distributions and Coriolis Coefficients for Extremal Force Constants in Bent XY_2, Pyramidal XY_3, and Tetrahedral XY_4 Molecules

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For 27 molecules with approximately extremal force fields, an empirical distinction between hydrides and non-hydrides is linked, via the comparison of calculated and observed Coriolis coefficients, to a difference, based ultimately on the relative lightness of the hydrogen atom, in the potential energy distributions of hydrides and non-hydrides. The potential energy criteria of Becher and Ballein are compared to those corresponding to extremal diagonal force constants. Coriolis coefficients for the model of progressive rigidity are mostly in rough agreement with those observed.

Introduction

Recently, papers have appeared[1, 2] dealing with the extremal properties of the vibrational force constants in the second order secular equation, the general solution of which is the subject of a rather thorough earlier treatment[3]. Only in the case of a secular equation of the second order does an extremum of either diagonal force constant procure a unique solution for the force field and normal coordinate transformation. From the results of STREY and KLAUSS[1] and of BECHER and BALLEIN[2] on the extremal force constants of a variety of molecules, the following two empirical statements may be made:

(a) One of the two extremal solutions (corresponding either to the maximal stretching force constant or to the minimal bending force constant) is often a fairly good approximation to the accurately determined force field.

(b) In such cases, a distinction exists between hydride and non-hydride molecules, in that for *all* of the latter the extremal solutions with maximal stretching force constants are never close to the accurately determined force fields.

The main point of the present note is to supplement the recent work on extremal force constants[1, 2] by correlating the above remark (b) to properties of the potential energy distributions and Coriolis coefficients for 27 molecules for which the remark (a) is true.

Discussion

(1) Vibrational potential energy distributions

The two distributions of potential energy among the symmetry force constants, corresponding to the force fields with maximal $F_{\sigma\sigma}$ (stretching) and mini-

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[1] G. STREY, J. Mol. Spectry. **24**, 87 [1967]. — G. STREY and K. KLAUSS, Z. Naturforsch. **23 a**, 1667, 1717 [1968].

[2] H. J. BECHER and K. BALLEIN, Z. physik. Chem. Frankfurt **54**, 302 [1967].

[3] P. TORKINGTON, J. Chem. Phys. **17**, 357 [1949].