



## Analytical formulae for the energy of electron subshells in atoms and their optimization

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**Abstract.** Generalized analytical orthonormal quasi-hydrogenic radial wave functions with free parameters (radius-dependent screened nuclear charge) are introduced. By them the analytical expressions for Slater radial integrals are derived. Using the Racah coefficients of partial parentage, the sequential formulae for branching fractions of equivalent electrons, incorporating  $LS$ -coupling of angular momenta inside terms of unfilled subshells, are proposed. Racah partial parentage or branching coefficients for the unfilled electron subshells are implicitly generated via the Pauli exclusion principle. The free parameters of the radial Slater integrals in Hamiltonian are proposed to be optimized by the Levenberg–Marquardt best-fit optimization version of the least squares method. To its cost function the virial ratio of kinetic and potential energy is added as a Lagrange constraint term. Thus, the solution of Hartree–Fock eigenvalue equations is proposed to be replaced by a nonlinear optimization method. The integrals in Hamiltonian correspond to the kinetic energy of electrons, their interaction with the atomic nucleus and electrostatic interaction between electrons. This interaction includes the Coulomb and exchange interaction between equivalent and non-equivalent electron pairs, including the multi-configurational interaction contribution. A general compact formula for  $6j$ -symbols is presented and used to describe the interaction of single excited electrons with electrons in filled or unfilled atomic subshells. It is proposed to realize generalization of the single configuration approach to a multi-configuration mixing in the  $n$ -dimensional Euclidean space, where the mixing coefficients are the polar direction cosines.

**Key words:** atomic subshells, analytical formulae, numerical optimization.

### 1. INTRODUCTION

A complicated but important topic in astrophysics is computation of stellar spectral lines of atoms and their ions. Theoretical physicists and astrophysicists both have puzzled over this topic. As a result of essential successes, extensive spectral line catalogues have been compiled, say, by Kurucz and Vienna astrophysicists, but much is to be done in order to elaborate more general, elegant, and uniquely treatable analytical formalism of high precision.

In order to elucidate the situation, we try to describe main milestones in the studies of atomic spectra, giving mainly references to essential summarizing monographs by prominent contributing theoreticians. The most important achievement and starting point is the Schrödinger equation for hydrogen atom and hydrogenic ions. This quantum mechanical equation gave a generalization of the Bohr atomic model. In it the electron moment was expressed as spatial derivative, scaled via the Planck constant in the central electrostatic field of proton. The differential equations with partial derivatives were a favourite topic in the problems of eigenfunctions and discrete eigenvalues, studied by many mathematicians, say by Laguerre,

Legendre, and Rodrigues. It turned out that the Schrödinger equation for hydrogen was directly connected with the eigenvalues and eigenfunctions studied by mathematicians.

In order to obtain solutions for more complicated atomic particles, the time-independent Schrödinger perturbation method and the time-dependent Dirac perturbation method were elaborated. Most spectral studies have been based on different versions of these methods.

The next essential step was generalization of the Schrödinger equation to the two-electron helium atom. No exact analytical solution to the problem was found, but the hydrogen wave functions have been modified in different ways. The most important summary of results in this direction is given in the monograph by Bethe and Salpeter (1957).

The Hamiltonian for the multi-particle atoms includes kinetic energy of electrons, potential energy of their interaction, and the electrostatic interaction with the nucleus. This equation must be solved as the first step in order to compute the line spectrum of atomic particles. The additives in the total energy, corresponding to this wave function, incorporate the classical direct and quantum theoretical exchange electrostatic interaction of electrons. In the Hamiltonian these additives incorporate the radial integrals, called the Slater orbital integrals, which are multiplied by the angular integrals, incorporating the Racah branching fractions. These fractions in the unfilled electron subshells are directly determined by the quadratic expressions of fractional parentage coefficients and by seniority numbers, for which the contribution by Racah (1942a, 1942b, 1943, 1949) has been dominant. A detailed review of the results of the theory of atomic spectra is given in the monograph by Sobelman (1972).

The Hartree–Fock equations (Hartree, 1957) for the radial wave functions are usually solved numerically using complicated multi-configurational approximation schemes (Froese Fischer et al., 2000). Different attempts have been made to find analytical approximation formulae for them, but these have remained hitherto without essential success. We hope that the present paper can help to promote the studies.

One of the important fields of quantum mechanics is the theory of the angular momenta, which started with the Clebsch–Gordan coefficients and  $3j$ -symbols, and evolved into the complicated  $nj$ -symbols theory for the addition of the multiple angular momenta (Jucys and Bandzaitis, 1977; Johnson, 2007). In the present paper we try partly to avoid the problems connected with the theory of the addition of angular momenta, using instead the Racah branching fractions for the unfilled subshells of atoms and ions. It should be mentioned that by a recurrent use of Racah branching fractions the problems connected with the seniority of spectral terms can be overcome.

## 2. RADIAL ORBITALS OF NON-HYDROGENIC ATOMS

For atoms and ions the quasi-hydrogenic form of radial wave functions or Slater orbitals for any subshell is (Kupliauskis et al., 1971; Sapor, 1973)

$$P_{nl} = \sum_{i=1}^{n-l} c_{ni}^l r^{i+l} e^{-Z_{ni}^l r}, \quad (1)$$

with is a generalization of the hydrogenic wave functions, where  $Z_{ni}^l = Z/n$ . Here radial functions are expressed in the Bohr atomic units.

The needed orthonormality constraint of radial wave functions is

$$Q_{nn'}^l = \int_0^\infty P_{nl} P_{n'l} dr = \delta_{nn'}, \quad l+1 \leq n' \leq n. \quad (2)$$

It can be written in the form

$$\sum_{i=1}^{n-l} c_{ni}^l b_{nin'}^l = \delta_{nn'}, \quad l+1 \leq n' \leq n, \quad (3)$$

where

$$b_{nin'}^l = \sum_{j=1}^{n'-l} c_{n'j}^l A_{nin'j}^l \quad (4)$$

and here in its turn

$$A_{nin'j}^l = \int_0^\infty r^k e^{-(Z_{ni}^l + Z_{n'j}^l)r} dr = \frac{k!}{(Z_{ni}^l + Z_{n'j}^l)^{k+1}}, \quad k = 2l + i + j. \quad (5)$$

The number of orthonormality conditions from (3) and (4) and the total number of coefficients  $c_{ni}^l$  are equal, namely  $\frac{1}{2}(n-l+1)(n-l)$ , and thus these coefficients can be found from the quadratic system of equations. Based on the constraint  $n' \leq n$  this system of equations can be reduced to a system of linear equations for finding consequently the  $c_{ni}^l$  values.

It is reasonable to split the system of equations (3) into two subsystems, the first of which corresponds to the case  $n' = n$  and gives the normalization condition

$$\sum_{i=1}^{n-l} c_{ni}^l b_{nin}^l = 1, \quad b_{nin}^l = \sum_{j=1}^{n-l} c_{nj}^l A_{ninj}^l, \quad l+1 \leq n \quad (6)$$

and the second corresponds to the cases  $n' < n$ , which are the orthogonality conditions of the radial wave functions:

$$\sum_{i=1}^{n-l} c_{ni}^l b_{nin'}^l = 0, \quad b_{nin'}^l = \sum_{j=1}^{n'-l} c_{n'j}^l A_{nin'j}^l, \quad l+1 \leq n' < n. \quad (7)$$

For simplicity it is useful to scale variables in Eqs (6) and (7) to the form

$$\beta_{nin'}^l = \frac{b_{nin'}^l}{c_{n1}^l}, \quad x_{ni} = \frac{c_{ni}^l}{c_{n1}^l}, \quad (8)$$

omitting explicitly indices  $l$ . Thus, Eq. (7) takes the form

$$\sum_{i=1}^{n-l} x_{ni} \beta_{nin'} = 0, \quad \beta_{nin'} = \sum_{j=1}^{n'-l} x_{n'j} A_{nin'j}^l, \quad n' < n \quad (9)$$

and the scaled form of normalization condition (6) is

$$c_{n1}^l \sum_{i=1}^{n-l} x_{ni} \beta_{nin} = 1, \quad \beta_{nin} = c_{n1}^l \sum_{j=1}^{n-l} x_{nj} A_{ninj}^l. \quad (10)$$

Due to the scaling we have  $x_{n1} = 1$ . Thus, orthogonality constraint (9) can be written in the form

$$\sum_{i=2}^m x_{ni} \beta_{nin'} = -\beta_{n1n'}, \quad m = n-l, \quad n' < n. \quad (11)$$

Now we can solve the orthogonality constraints (11), starting from  $m = 2$  and getting values of all scaled variables  $x_{ni}$  and  $\beta_{nin'}$ .

Thereafter the scaling factors  $c_{n1}^l$  are found from normalization conditions

$$(c_{n1}^l)^2 \sum_{i=1}^m \sum_{j=1}^m A_{nin'j}^l x_{ni} x_{nj} = 1, \quad m = n-l. \quad (12)$$

If all values of  $x_{ni}$  are found, then the quantities  $c_{ni}^l$  can be found trivially from  $c_{ni}^l = x_{ni} c_{n1}^l$ .

The quasi-hydrogenic orbitals guarantee also conservation of the node numbers in orbitals similarly to results of computations by the Hartree–Fock method. If we have the analytical orthonormal orbitals, it will be simpler to apply the variational minimum principle for the energy expression, avoiding the necessity of non-diagonal terms and Lagrangian coefficients to guarantee orthogonality of radial orbitals for different values of principal quantum numbers  $n$ .

### 3. ENERGY INTEGRALS OF ATOMIC PARTICLES

The energy of electrons in each atomic subshell, specified by  $\iota = nl$ , consists of three contributions: the kinetic energy of electrons and the potential energy due to the interaction of electrons with the atomic nucleus, together denoted as  $I_\iota$ , and the most complicated contribution by the electrostatic repulsive interaction between electrons. The total energy over all  $M$  interacting subshells is

$$E = \sum_{\iota=1}^M E_\iota + \sum_{\iota=2}^M \sum_{\tau=1}^{\iota-1} E_{\iota\tau}. \quad (13)$$

The intrinsic energy of any filled or unfilled subshell  $\iota$  specified by configuration  $nl^{N_\iota}$ , having  $N_\iota$  equivalent electrons, in the single configuration approximation is

$$E_\iota = N_\iota I_\iota + \frac{N_\iota(N_\iota - 1)}{2} F_{\iota\iota}^0 - \frac{N_\iota(N_\iota - 1)}{2} \sum_{k=2,4,\dots}^{2l_\iota} f_{\iota\iota}^k F_{\iota\iota}^k, \quad (14)$$

where  $F_{\iota\iota}^k$  specifies the averaged interaction energy by pairs of equivalent electrons.

The electrostatic energy between two subshells  $\iota$  and  $\tau$  due to the direct or Coulomb interaction and due to the exchange interaction is

$$E_{\iota\tau} = N_\iota N_\tau F_{\iota\tau}^0 - N_\iota N_\tau \sum_{k=|l_\iota - l_\tau|}^{l_\iota + l_\tau} g_{\iota\tau}^k G_{\iota\tau}^k, \quad \iota > \tau. \quad (15)$$

In these formulae the integrals  $F_{\iota\tau}^k$  and  $G_{\iota\tau}^k$  are the radial direct and exchange Slater integrals, respectively. The values of angular coefficients  $f_{\iota\iota}^k$  and  $g_{\iota\tau}^k$  for the filled subshells can be expressed in the form

$$f_{\iota\iota}^k = \frac{N_\iota}{N_\iota - 1} \Lambda_{\iota\iota}^k, \quad k = 2, \dots, 2l_\iota \quad (16)$$

and

$$g_{\iota\tau}^k = \Lambda_{\iota\tau}^k. \quad (17)$$

In these formulae the interaction unit  $\Lambda_{\iota\tau}^k$  is expressed via the reduced  $3j$ -symbol defined by

$$\langle l_\iota || C^k || l_\tau \rangle = [l_\iota] \begin{pmatrix} l_\iota & k & l_\tau \\ 0 & 0 & 0 \end{pmatrix} [l_\tau], \quad [l_\iota] = \sqrt{2l_\iota + 1}, \quad [l_\tau] = \sqrt{2l_\tau + 1} \quad (18)$$

in the form

$$2\Lambda_{\iota\tau}^k = \left( \frac{\langle l_\iota || C^k || l_\tau \rangle}{[l_\iota][l_\tau]} \right)^2 = \left( \begin{pmatrix} l_\iota & k & l_\tau \\ 0 & 0 & 0 \end{pmatrix} \right)^2. \quad (19)$$

The contribution by  $k > 0$ , i.e. due to multipole contribution of terms, reduces somewhat the Coulomb repulsion between electrons. Denoting  $2g = l_1 + l_2 + l_3$  and  $\delta e(2g) = \frac{1+(-1)^{2g}}{2}$ , we can write compactly the expression (cf. Johnson, 2007, equation (1.85)) that removes automatically the odd values of the summed orbital parameters  $2g$ , namely

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} = \delta e(2g) (-1)^g \frac{g!}{\sqrt{(2g+1)!}} W_1 W_2 W_3, \quad (20)$$

where  $W_j = \frac{\sqrt{(2g-2l_j)!}}{(g-l_j)!}$ .

#### 4. RADIAL SLATER INTEGRALS OF NON-HYDROGENIC ATOMS

The needed unshielded Slater integrals in the energy Hamiltonian are

$$I_i = I_{nl} = -\frac{1}{2} \int_0^\infty P_{nl}(r) \left( \frac{d^2}{dr^2} + \frac{2Z^+}{r} - \frac{l(l+1)}{r^2} \right) P_{nl}(r) dr = -\frac{1}{2} \left( D^2 + \frac{2Z^+}{\bar{r}^1} - \frac{l(l+1)}{\bar{r}^2} \right), \quad (21)$$

where  $Z^+$  is the nuclear charge. Further, for the compactness of formulae, we here denote in  $P_{nl}(r)$  expressions

$$C_i = c_{nli}, \quad Z_i = Z_{ni}^l. \quad (22)$$

Taking into account that  $\int_0^\infty r^S e^{-Zr} dr = S!/Z^{S+1}$ , we obtain

$$D^2 = \sum_{i=1}^{n-l} \sum_{j=1}^{n-l} C_i C_j \left( \frac{\kappa! Z_j^2}{Z_{ij}^{\kappa+1}} - \frac{2Z_{nlj}(l+j)(\kappa-1)!}{Z_{ij}^\kappa} + \frac{(l+j)(l+j-1)(\kappa-2)!}{Z_{ij}^{\kappa-1}} \right), \quad (23)$$

where  $Z_{ij} = Z_i + Z_j$  and  $\kappa = 2l + i + j$ . Further

$$\frac{1}{\bar{r}^1} = \sum_{i=1}^{n-l} \sum_{j=1}^{n-l} C_i C_j \frac{(\kappa-1)!}{Z_{ij}^\kappa}, \quad \text{and} \quad \frac{1}{\bar{r}^2} = \sum_{i=1}^{n-l} \sum_{j=1}^{n-l} C_i C_j \frac{(\kappa-2)!}{Z_{ij}^{\kappa-1}}. \quad (24)$$

As an important generalization for the theory of spectral lines, the radial integrals of the  $k$  order electron multipole transition probabilities can be expressed by integrals

$$I_{nl'n'l'}^k = \int_0^\infty P_{nl}(r) r^k P_{n'l'}(r) dr = \sum_{i=1}^{n-l} \sum_{j=1}^{n-l} C_i C_j \frac{S_{ij}!}{(Z_{ij})^{S_{ij}+1}}, \quad (25)$$

where

$$S_{ij} = n + l + i + k + n' + l' + j, \quad Z_{ij} = Z_{ni}^l + Z_{n'j}^{l'}. \quad (26)$$

The total electrostatic interaction of electrons for the direct interaction is to be found by radial integrals

$$F_{nn'}^k = R_{nn',n'n'}^{kl'l'} = \int_0^\infty \int_0^\infty P_{nl}^2(r) \frac{r_{<}^k}{r_{>}^{k+1}} P_{n'l'}^2(s) dr ds \quad (27)$$

and for the exchange interaction by

$$G_{nn'}^k = R_{nn',nn'}^{kl'l'} = \int_0^\infty \int_0^\infty P_{nl}(r) P_{n'l'}(r) \frac{r_{<}^k}{r_{>}^{k+1}} P_{nl}(s) P_{n'l'}(s) dr ds. \quad (28)$$

Here  $r_{<} = \min(r, s)$  and  $r_{>} = \max(r, s)$ . The needed special cases of these integrals of the direct and exchange interaction of electrons in the total energy of electron subshells have been given in formulae (14) and (15). Due to the symmetry of integrals relative to subshells we can assume that  $n \geq n'$ .

For the direct interaction Slater integrals reduce to

$$R_{nn',n'n'}^{kl'l'} = \sum_{i=1}^{n-l} \sum_{p=1}^{n-l} \sum_{j=1}^{n-l} \sum_{q=1}^{n-l} C_i C_p C_j C_q K_{bd}^k(Z, \zeta). \quad (29)$$

Here the integrals obtained by the multiplication of two radial Slater orbitals are

$$K_{bd}^k(Z, \zeta) = \int_0^\infty \int_0^\infty e^{-Zr} r^b \frac{r^k}{r^{k+1}} e^{-\zeta s} s^d dr ds, \quad (30)$$

where the parameters and variables of integrals are linear sums of single Slater orbitals, namely

$$b = 2l + i + p, \quad d = 2l' + j + q, \quad Z = Z_{ni}^l + Z_{np}^l \quad \zeta = Z_{n'j}^{l'} + Z_{n'q}^{l'} \quad (31)$$

and for the superscripts  $k$  holds the constraint  $k \leq l + l'$ .

Next we find analytical expressions to the Slater radial integrals. Now we can write

$$K_{bd}^k(Z, \zeta) = \int_0^\infty e^{-\zeta s} \frac{s^d}{s^{k+1}} ds \int_0^s e^{-Zr} r^{b+k} dr + \int_0^\infty e^{-Zr} \frac{r^b}{r^{k+1}} dr \int_0^r e^{-\zeta s} s^{d+k} ds. \quad (32)$$

The first integration gives

$$\int_0^s e^{-Zr} r^m dr = \frac{m!}{Z^{m+1}} \left( 1 - e^{-Zs} \sum_{i=0}^m \frac{Z^i s^i}{i!} \right), \quad m = b + k. \quad (33)$$

Denoting  $g = d - k - 1$  we can write the result of the second integration in the form

$$I_{bd}^k(Z, \zeta) = \int_0^\infty e^{-\zeta s} s^g ds \int_0^s e^{-Zr} r^m dr = \frac{m!}{Z^{m+1}} \left( \frac{g!}{\zeta^{g+1}} - \sum_{i=0}^m \frac{(g+i)! Z^i}{i! (\zeta + Z)^{g+i+1}} \right). \quad (34)$$

Thus we have found analytical expressions for the integrals of direct interaction

$$K_{pq}^k(Z, \zeta) = I_{bd}^k(Z, \zeta) + I_{db}^k(\zeta, Z). \quad (35)$$

For the exchange interaction the Slater integrals reduce to similar expressions

$$R_{nn',nn'}^{kl'l'} = \sum_{i=1}^{n-1} \sum_{q=1}^{n'-1} \sum_{j=1}^{n'-1} \sum_{p=1}^{n-1} C_i C'_q C'_j C_p K_{b'd'}^k(Z', \zeta'), \quad (36)$$

where the integrals of the exchange interaction can be written in the same form as for the direct interaction

$$K_{b'd'}^k(Z', \zeta') = \int_0^\infty \int_0^\infty e^{-Z'r} r^{b'} \frac{r^k}{r^{k+1}} e^{-\zeta' s} s^{d'} dr ds, \quad (37)$$

but with different parameters

$$b' = l + l' + i + q, \quad d' = l + l' + j + p, \quad Z' = Z_{ni}^l + Z_{n'q}^{l'}, \quad \zeta' = Z_{n'j}^{l'} + Z_{np}^l. \quad (38)$$

By using notions  $g' = d' - k - 1$ ,  $m' = b' + k$  the expressions of integrals for the exchange interaction can be expressed in the form

$$K_{b'd'}^k(Z', \zeta') = I_{b'd'}^k(Z', \zeta') + I_{d'b'}^k(\zeta', Z'). \quad (39)$$

Thus, we have carried out an analytical integration of all radial Slater integrals needed in the single configuration approximation.

We give here also an analytical expression for an average radial screening charge,  $Z_{sc}(r)$ . Using Eqs (1) and (33), we obtain

$$Z_{sc}(r) = N_l \int_0^r P_{nl}^2(\rho) d\rho = N_l \sum_{i=1}^{n-l} \sum_{p=1}^{n-l} C_i C_p K_m(Z, r), \quad (40)$$

where  $N_l$  is the number of electrons in the subshell  $l$  and

$$K_m(Z, r) = \frac{m!}{Z^{m+1}} \left( 1 - e^{-Zr} \sum_{j=0}^m \frac{Z^j r^j}{j!} \right), \quad m = 2l + i + p, \quad Z = Z_{ni}^l + Z_{np}^l. \quad (41)$$

## 5. SPECTRAL TERMS OF UNFILLED SUBSHELLS

Partly the spectral terms  $^{2S+1}L$  of unfilled electron subshells of atomic particles are singled out by the Pauli exclusion principle, demanding lack of electrons with identical set of quantum numbers. We use the spin-orbital or the  $LS$ -coupling concept of electron angular momenta, which holds for lighter chemical elements. The subshells for which  $n$  is the same but the orbital quantum number  $l$  has values  $l = [0, n-1]$  belong to the shell of principal quantum number  $n$ . Corresponding spherical harmonics  $Y_{lm}$  have  $2l+1$   $z$ -components,  $m_l = [-l, l]$ , and in addition each electron can have two  $z$ -coordinate projections of spin,  $m_s = [\frac{1}{2}, -\frac{1}{2}]$ . Thus, the maximal number of electrons in such subshells is  $T_l = 2(2l+1)$ . If the occupation or population number of a subshell is  $p$ , then the number of possible different microstates in any subshell according to the Pauli exclusion principle is

$$N_l^p = \frac{T_l!}{p!(T_l-p)!}. \quad (42)$$

The same number of quantum states for any subshell can be expressed also as the sum over the states of spectral terms  $i$

$$N_l^p = \sum_i^{\kappa} (2S_i + 1)(2L_i + 1). \quad (43)$$

All the filled subshells have only a single term  $^1S$ . Also the terms for singly occupied subshells are trivial:  $^2S$ ,  $^2P$ ,  $^2D$ ,  $^2F$ ,  $^2G$ , etc.

The angular parts of terms generate the splitting of their binding energies. Degeneracy of splitting relative to  $m_l$  and  $m_s$  can be removed only due to the presence of a magnetic field, inherent because of the atomic nucleus or some external source.

Now we present for different configurations their terms and  $N_l^p$  values, starting from the  $p$ -subshell. The  $p^2$  configuration has the terms  $^1D$ ,  $^3P$ , and  $^1S$ . The total number of its states is  $N = 15$ . The doubly and triply coinciding terms in the  $d$  configuration belong to different seniorities  $\nu$ , shown by subscripts before the  $L$  values. If its place is blank, then  $\nu = n$ .

In order to describe the unfilled configurations compactly, we introduce for them notations  $l^n(N)$  and  $L^n(\kappa)$ , where  $L = l$  for counting the terms, here numerated by  $\kappa$ . Using these notations, we have

$$\begin{aligned} p^2(15) &= (^1D, ^3P, ^1S) = P^2(3), \\ p^3(20) &= (^2D, ^2P, ^4S) = P^3(3), \\ d^2(45) &= (^1G, ^3F, ^1D, ^3P, ^1S) = D^2(5), \\ d^3(120) &= (^2H, ^2G, ^4F, ^2F, ^2_1D, ^2_3D, ^4P, ^2P) = D^3(8), \\ d^4(210) &= (^1I, ^3H, ^3G, ^1_2G, ^1_4G, ^3_2F, ^3_4F, ^1F, ^5D, ^3D, ^1_2D, ^1_4D, ^3_2P, ^3_4P, ^1_0S, ^1_4S) = D^4(16), \\ d^5(252) &= (^2I, ^2H, ^4G, ^2_3G, ^2G, ^4_3F, ^2_3F, ^2_5F, ^4D, ^2_1D, ^2_3D, ^2_5D, ^4_3P, ^2_3P, ^6S, ^2S) = D^5(16), \\ f^2(91) &= (^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S) = F^2(7). \end{aligned}$$

The current value of any subscript of terms starts from the right hand; for example,  $D_1^3 = {}^2P$ . The unfilled lanthanide and actinide  $f$ -subshells with a larger population are very complicated and dominated by  $jj$ -coupling. Therefore these are not analysed by us.

For the terms of all configurations the electron-hole duality principle holds. The filling order of ground state subshells in the Mendeleev periodic table of elements is described by the well-known Bohr's Aufbau rule detailed by the Madelung energy ordering ( $n+l$ ) rule. For valence electron terms of the configurations of a partly filled subshell the ordering in the ground state is determined by Hund's selection rules that hold for the Russell-Sounders or  $LS$ -coupling.

## 6. ANGULAR INTEGRALS OF INTERACTING SPECTRAL TERMS

Spectral terms of unfilled subshells generate additional splitting of atomic states due to Racah angular integrals of the direct interaction in a subshell  $\iota$ , denoted by  $f_{\iota\iota}^k$ , and of the exchange interaction,  $g_{\iota\tau}^k$ , between subshells  $\iota$  and  $\tau$ . The splitting depends on the quantum numbers of terms  $T = l^i \nu SL$ , where  $\nu$  is the seniority number. We try to give the formulae for these angular integrals in a possibly compact form instead of the usual complicated ones.

We start from formulae for electron pair interaction. The general formulae for angular integrals of the electron pair in a term  $l'l'SL$  with angular momentum  $L$  can be expressed in the form that is the product of subshells-dependent and term-dependent parts. For the direct interaction holds (cf. Sobelman, 1972, equation (17.44); Johnson, 2007, equation (4.50))

$$f^{kL}(l'l') = (l||C^k||l)(l'||C^k||l')\phi^{kL}(l'l'), \quad \phi^{kL}(l'l') = (-1)^{l+l'+L} \left\{ \begin{matrix} l & l' & L \\ l' & l & k \end{matrix} \right\} \quad (44)$$

and for the exchange interaction of electron pairs (cf. Sobelman, 1972, equation 17.45)

$$g^{kL}(l'l') = -(l||C^k||l')^2\gamma^{kL}(l'l'), \quad \gamma^{kL}(l'l') = (-1)^{l+l'+S} \left\{ \begin{matrix} l & l' & L \\ l & l' & k \end{matrix} \right\}. \quad (45)$$

In these formulae the triangular rule  $|l-l'| \leq L \leq l+l'$  holds, and the multiplier  $(-1)^S$  of the phase sign generates different signs to singlet and triplet terms of a pair of electrons if  $l=l'$ . This formula corresponds to the Hund rule for the ground state,  $S=1$ , of two-electron spectral terms.

The fractional parentage coefficients (genealogical coefficients) of atomic states were conceptually introduced for the partially filled  $LS$ -coupled subshells by Goudsmit and Bacher (1934). Thereafter Racah (1942a, 1942b, 1943) elaborated a complicated, predominantly algebraic theory for the computation of angular integrals of  $p$  and  $d$  subshell electrons. In these papers he also tabulated the coefficients for the unfilled  $p$ ,  $d$  subshells. Thereafter Racah (1949) published an elegant Lie group theoretical study, in which  $f$  subshells were included. For these subshells a full list of the coefficients was published by Nielson and Koster (1963).

The Racah coefficients are determined for the study of unfilled atomic multi-electron subshells. We denote here the Racah overlap coefficients between terms of electron configurations  $l^\kappa$  and  $l^\lambda$ , where  $\lambda = \kappa + 1$ , of an unfilled subshell by  $G_\kappa^\lambda$ . The corresponding redistribution or Racah branching (ramification) fractions  $W_\kappa^\lambda$ , according to quantum mechanics, are given by

$$W_\kappa^\lambda = (G_\kappa^\lambda)^2. \quad (46)$$

The Pauli exclusion principle, including for the spin states, has been taken into account implicitly via the allowed terms in a given partially filled subshell.

The fractional parentage coefficients can be treated as the quantum mechanical probability redistribution amplitudes between interacting equivalent electrons, whereas the normalization condition for each subsequent branching holds

$$\sum_{\kappa} W_{\kappa}^{\lambda} = 1. \quad (47)$$

This equation demonstrates well the meaning of Racah fractions as redistribution coefficients between terms of two consequent configurations of equivalent electrons in unfilled subshells. We accept that a reasonable approximation to angular coefficients of equivalent electrons can be interpreted in this way. An important feature is that the Racah branching factors do not depend on the  $z$ -components of  $L$  and  $S$  and on the multipole index  $k$ .

In spectral terms in addition to  $lSL$  also the Racah seniority quantum numbers,  $\nu$ , which appear due to the Pauli principle and generate spectral lines splitting, must generally be taken into account to obtain orthonormality of the corresponding wave functions. It deserves emphasizing that for single electrons  $\nu = 1$ . Similarly to the spin, it is reasonable to introduce the seniority phase functions

$$\Psi(\nu\phi) = \frac{1}{\sqrt{2\pi}} e^{i\nu\phi}, \quad (48)$$

which guarantee the orthonormality conditions of the corresponding wave functions

$$\int_0^{2\pi} \Psi^*(\nu\phi) \Psi(\nu'\phi) d\phi = \delta_{\nu\nu'}. \quad (49)$$

Now we can write for seniority modified wave functions recurrent formulae

$$\Phi_j = \sum_{j-1} \Psi(\nu_{j-1}\phi) G_{j-1}^j \Phi_{j-1}, \quad (50)$$

which satisfy the conditions of orthonormality for different terms of an unfilled subshell:

$$\int_0^{\pi} d\vartheta \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \Phi_i \Phi_j = \delta_{ij}. \quad (51)$$

The total Racah redistribution coefficients, connecting the network branches with the initial term of the electron pair interaction is given by recurrent equations

$$W_2^i = \sum_j W_j^i W_2^j, \quad T_i = T_{j+1}. \quad (52)$$

Summation here is over the terms of configuration  $l^j = l^{i-1}$  and  $i$  is the set of  $l^i$  configuration terms. This quantity is independent of the multipole index  $k$ . Via subscript 2 it is dependent on the initial electron pair interaction terms and the corresponding spectral shifts. The number of these multi-step ramification coefficients is relatively small and therefore these ramification coefficients can be easily tabulated.

From Eq. (52) it follows that the Racah angular integrals of interacting  $l^i l^j$  configuration electrons are

$$f_i^k = W_2^i f^{kL}(ll'), \quad g_i^k = W_2^i g^{kL}(ll'). \quad (53)$$

Due to the particle-hole symmetry the spectral terms relative to  $i = l + 1 \pm m$  in subshells are coincident ones, but they have different, simply connected Racah branching fractions and different interacting electron pair numbers.

Next we give in a compact form a general expression for 6j-symbols, using the triangle coefficients

$$\Delta(j_1 j_2 j_3) = \left( \frac{(2S - 2j_1)!(2S - 2j_2)!(2S - 2j_3)!}{(2S + 1)!} \right)^{1/2}, \quad 2S = j_1 + j_2 + j_3. \quad (54)$$

To simplify the formulae, it is useful to write the Wigner 6j-symbol in the form

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ q_1 & q_2 & q_3 \end{array} \right\} \equiv \left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{array} \right\} \quad (55)$$

and to introduce notations

$$J_i = j_i + q_i, \quad J = \sum_{i=1}^3 J_i, \quad q = \sum_{i=1}^3 q_i, \quad j = \sum_{i=1}^3 j_i, \quad y_i = q - q_i + j_i, \quad w_i = J - J_i. \quad (56)$$

Using these parameters we obtain a relatively simple formula (cf. Johnson (2007), formula (4.38))

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ q_1 & q_2 & q_3 \end{array} \right\} = \Delta \sum_{z=z_{\min}}^{z_{\max}} (-1)^z \frac{(z+1)!}{Q_z Y_z}, \quad (57)$$

where the triangular coefficient

$$\Delta = \Delta(j_1 j_2 j_3) \Delta(j_1 q_2 q_3) \Delta(q_1 j_2 q_3) \Delta(q_1 q_2 j_3) \quad (58)$$

and the weight coefficients in denominators are

$$Q_z = (z-j)! \prod_{i=1}^3 (z-y_i)!, \quad Y_z = \prod_{i=1}^3 (w_i - z)!. \quad (59)$$

The limits of summation are here specified by

$$z_{\max} = \min(w_1, w_2, w_3), \quad z_{\min} = \max(j, y_1, y_2, y_3). \quad (60)$$

For the exchange interaction of terms of an electron pair (45), diminishing  $z$  by  $l+l'$ , it follows that

$$\left\{ \begin{array}{ccc} l & l' & L \\ l & l' & k \end{array} \right\} = \Delta \sum_{z=\max(L,k)}^{z_{\max}} \frac{(-1)^{z+l+l'} (z+l+l'+1)!}{Q_z Y_z}, \quad (61)$$

where

$$Q_z = (z-L)!^2 (z-k)!^2, \quad Y_z = (l-l'+L+k-z)! (l'-l+L+k-z)! (l+l'-z)!. \quad (62)$$

Here  $z_{\max} = \min(L+k-|l-l'|, l+l')$  and the triangular part is

$$\Delta = \Delta^2(l'l'L) \Delta^2(l'l'k) = \frac{(l+l'-L)! (l+l'-k)! (l-l'+L)!^2 (l-l'+k)!^2}{(l+l'+L+1)! (l+l'+k+1)!}. \quad (63)$$

From Eqs (61) and (63) it follows that  $|l-l'| \leq k \leq l+l'$  and  $|l-l'| \leq L \leq l+l'$ .

For the direct interaction of electron pair (44) we obtain similarly

$$\left\{ \begin{array}{ccc} l & l' & L \\ l' & l & k \end{array} \right\} = \Delta \sum_{z=\max(k-|l-l'|, L)}^{\min(L+k, l+l')} \frac{(-1)^{z+l+l'} (z+l+l'+1)!}{(z-L)!^2 (z-k+|l-l'|)!^2 (L+k-z)!^2 (l+l'-z)!}. \quad (64)$$

Here  $\Delta$  is the same as for the exchange interaction of electron pairs of different subshells. Thus, relative separation of such direct and exchange terms does not depend on the triangular part.

For the case  $l = l'$

$$\left\{ \begin{array}{ccc} l & l & L \\ l & l & k \end{array} \right\} = C(2l, L) C(2l, k) \sum_{z=\max(L,k)}^{\min(L+k, 2l)} \frac{(-1)^z (z+2l+1)!}{(z-L)!^2 (z-k)!^2 (L+k-z)!^2 (2l-z)!}, \quad (65)$$

where the triangular part

$$\Delta = C(2l, L)C(2l, k) = \frac{L!^2(2l - L)! k!^2(2l - k)!}{(2l + L + 1)! (2l + k + 1)!}. \tag{66}$$

From here it also follows that  $L \leq 2l$  and  $k \leq 2l$ . For special cases if  $Lk = 0$ , we have  $z = 0$  and

$$\left\{ \begin{matrix} l & l & L \\ l & l & 0 \end{matrix} \right\} = \left\{ \begin{matrix} l & l & 0 \\ l & l & k \end{matrix} \right\} = \left\{ \begin{matrix} l & l & 0 \\ l & l & 0 \end{matrix} \right\} = \frac{1}{2l + 1} = \frac{1}{[l]^2}. \tag{67}$$

In addition to the recurrent formulae by the Racah branching coefficients, there are important formulae for diagonalized quantum states in Hamiltonian, corresponding thus to the eigenvalue problems.

The total splitting of energy states due to Coulomb interaction of electrons in  $l^n$  configuration between the terms  $T = \nu SL$  and  $T' = \nu' SL'$  according to Sobelman (1972, cf. (18.22)) is per term

$$f^{kL}(l^n) = \frac{1}{2} \langle l || C^k || l \rangle^2 \left[ \frac{n^2}{[L]^2} \sum_{T'} \langle T || U^k || T' \rangle^2 - \frac{n}{2l + 1} \right]. \tag{68}$$

Total Hamiltonian incorporates summation over all these energetically shifted terms of configuration  $l^n$ . The angular overlap integral, corresponding to the Coulomb interaction of equivalent electrons, is

$$\langle T || U^k || T' \rangle = n \sum_{T_1} G_{T_1}^T G_{T_1}^{T'} (-1)^{L_1 + k - l - L} [L][L'] \left\{ \begin{matrix} l & L & L_1 \\ L' & l & r \end{matrix} \right\}, \quad |L - l| \leq L_1 \leq L + l. \tag{69}$$

Here the triangular coefficient

$$\Delta = \Delta(lLL_1)\Delta(lLk)\Delta(L'Lk)\Delta(L'lL_1). \tag{70}$$

Next we give formulae for the interaction of the  $l^n$  and  $l'$  configuration terms  $T_1 = \nu_1 S_1 L_1$  and  $T' = \frac{1}{2} l'$ . For them we summarize on the basis of formulae by Sobelman (1972, §18) that

$$f_{T_1 T'}^k = \langle l || C^k || l \rangle \langle l' || C^k || l' \rangle (-1)^{L_1 + l' - L} \langle T_1 || U^k || T_1 \rangle \left\{ \begin{matrix} L_1 & l' & L \\ l' & L_1 & k \end{matrix} \right\} \tag{71}$$

and

$$g_{T_1 T'}^k = -\langle l || C^k || l' \rangle^2 \sum_{r=|l-l'|}^{|l+l'|} (-1)^r (2r + 1) \left\{ \begin{matrix} l & l & r \\ l' & l' & k \end{matrix} \right\} (A_{T_1 l'}^r + B_{T_1 l'}^r). \tag{72}$$

The tensor elements in brackets are

$$A_{T_1 l'}^r = \frac{1}{2} (-1)^{L_1 + l' - L} \langle T_1 || U^r || T_1 \rangle \left\{ \begin{matrix} L_1 & l' & L \\ l' & L_1 & r \end{matrix} \right\} \tag{73}$$

and

$$B_{T_1 l'}^r = 2(-1)^{L_1 - L + S_1 - S + l' + 1/2} \sqrt{\frac{3}{2}} \langle T_1 || V^{1r} || T_1 \rangle \left\{ \begin{matrix} L_1 & l' & L \\ l' & L_1 & r \end{matrix} \right\} \left\{ \begin{matrix} S_1 & 1/2 & S \\ 1/2 & S_1 & 1 \end{matrix} \right\}. \tag{74}$$

Here the allowed values of final quantum numbers, according to the addition of angular momenta, are

$$S = S_1 \pm 1/2, \quad |L_1 - l'| \leq L \leq L_1 + l'. \tag{75}$$

The matrix elements of the spin interaction dependent tensor operator  $V^{1r}$ , having rank  $r$  relative to spin and  $-r$  relative to  $L$ , are

$$\langle T_1 || V^{1r} || T_1 \rangle = n \sum_{T_2} G_{T_2}^{T_1} G_{T_2}^{T_1} (-1)^j \sqrt{\frac{3}{2}} [L_1]^2 [S_1]^2 \left\{ \begin{matrix} l & L_1 & L_2 \\ L_1 & l & r \end{matrix} \right\} \left\{ \begin{matrix} 1/2 & S_1 & S_2 \\ S_1 & 1/2 & 1 \end{matrix} \right\}. \tag{76}$$

The summary phase sign  $j$  and the values of final quantum numbers are here specified by

$$j = l + L_1 - L_2 + 1/2 + S_1 - S_2 + r + 1, \quad S_2 = S_1 \pm 1/2, \quad |L_1 - l| \leq L_2 \leq L_1 + l. \quad (77)$$

The contribution due to spin is given by the  $6j$ -coefficients

$$\left\{ \begin{array}{ccc} S_1 & 1/2 & S \\ 1/2 & S_1 & 1 \end{array} \right\} = \Delta \sum_{z=z_{\min}}^{z_{\max}} \frac{(-1)^z (z+1)!}{Q_z Y_z}, \quad (78)$$

where the limiting functions are

$$Q_z = (z - S_1 - S - 1/2)! (z - 1 - 2S_1)! (z - 2)!, \quad Y_z = (S + S_1 + 3/2 - z)! (2S_1 + 1 - z)!. \quad (79)$$

The values of limiting quantum numbers are here

$$z_{\min} = \max(2S_1 + 1, S + S_1 + 1/2), \quad z_{\max} = \min(2S_1 + 1, S + S_1 + 3/2). \quad (80)$$

The triangular coefficient in this case is

$$\Delta = \Delta^2(S_1, 1/2, S) \Delta^2(S_1, 1/2, 1). \quad (81)$$

We note once more that in these formulae both the electrostatic  $U^k$  and spin  $V^{1r}$  interaction terms are diagonalized.

Two unfilled ground state subshells have of neutral atoms only Cr ( $3d^5 4s$ ), Mo ( $4d^5 5s$ ), and some lanthanides, whereas both of these subshells have single electron subshell terms. The problem is more complicated for highly ionized atoms, where the valence electrons have high velocities, and thus additional relativistic perturbational corrections are essential. In the study of stellar spectra the high-stage or multiple ions are not needed, whereas temperatures in the modelling of stellar atmospheres are limited to about  $10^5$  K.

## 7. PROPOSED MODIFIED COMPUTATIONAL METHODS

In the present section we sketch further, dominantly computational aspects for the application of the formulae given in the present paper.

The concept of constructing the single configuration wave functions is based on the analogy with the states of hydrogenic atoms. The uniquely fixed quantities of unfilled subshells of complex atoms and ions are the quantum numbers  $^{2S+1}L$  of terms and their configuration  $l^n$ . The formulae of single configuration approximation in many cases have too low precision, demanding to apply multi-configurational concept. This improvement of approximation for spectroscopy was first proposed and applied by Jucys (1952). This generalization of formulae means that the former atomic states are generalized to the linear combination of the same term states, having the same number of particles but different  $l$  values. Also such mixed states must be normalized. This is a constraint to new multi-configurational wave functions, which demands to introduce the mixing coefficients  $C_i$  of different configuration states. We propose to parameterize these as generalized direction cosines on the multi-configurational unit-sphere in polar coordinates of the  $n$ -dimensional Euclidean space by recurrence formulae

$$C_1 = \cos \theta_1, \quad C_i = \cos \theta_i S_{i-1}, \quad S_i = \prod_{k=1}^i \sin \theta_k, \quad C_n = \prod_{k=1}^n \sin \theta_k, \quad \sum_{i=1}^n C_i^2 = 1. \quad (82)$$

The sum of squared mixing coefficients  $C_i$  is intrinsically normalized. In the single configuration approach  $\theta_i = 0$  for all values of  $i$ . Thus in this case  $C_1 = 1$  and  $C_i = 0$  if  $i > 1$ .

In a multi-configuration approximation the state functions for any term  $T_k$  are defined by

$$\Phi(T_k) = \sum_{i=1}^n C_i \Phi_i(T_k). \quad (83)$$

The corresponding multi-configurational contribution to energy,  $E_M$ , is given by a sum over all corresponding spectral terms

$$E_M = \sum_{T_k} E(T_k), \quad E(T_k) = \sum_{i,j=1}^n C_i C_j E_{ij}(T_k), \quad (84)$$

where subscripts  $i$  and  $j$  denote the mixed single configurations and  $k$  the terms of mixed configurations.

The proposed choice of mixing coefficients removes the necessity to solve any additional secular equation for the non-diagonal contribution of mixed subshells and guarantees automatically normalization constraint of mixed states. The values of the final improved polar angles  $\theta_i$  correspond to the variational minimum of energy. Multi-configurational radial Slater integrals can be generalized trivially, ascribing different subshells even up to four interacting and thereby correlating radial Slater orbitals.

The Racah branching fractions concept must hold also for mixed configuration spectral terms like in the case of the single configuration approach. Generally different radial Slater integrals can be ascribed to each term of mixed configuration.

The best way to specify the values of free constants in orbitals is to apply the Levenberg–Marquardt nonlinear optimization algorithm of the least-squares method applied to the Hamiltonian of binding energy. We have used such method successfully for modelling stellar atmospheres and their spectra (Sapar et al., 2013a, 2013b).

The expression to be minimized is

$$Q = \left( \frac{E}{E_{\text{obs}}} - 1 \right)^2 + \left( \frac{E}{E_{\text{kin}}} + 1 \right)^2. \quad (85)$$

This means that we try to obtain the best fit of the computed energy to its observed value  $E_{\text{obs}}$ , using as an additional Lagrange term the virial theorem about the ratio of the kinetic energy to the total negative binding energy.

In order to avoid the Lagrange conditions in the cost function of best-fit optimization, orthonormality constraints (2) must be solved also for the ‘virtual’ states between occupied and excited states. In this manner a new best-fit node in radial sign-alternating parts of wave functions will be generated for each next value of principal quantum number  $n$ .

It is essential to choose rationally the subshells for which the energy is to be minimized. The most correct way to carry out computations of energies relative to the bare nucleus is using the sum of ionization energies. However, for large values of nuclear charge  $Z$  the needed data are hitherto lacking and therefore such methods that do not need a priori numerical energy values are to be applied or some of the inner filled subshells can be treated as the inactive ones.

Thus, we propose not to solve exactly approximate eigenvalue equations but to minimize the binding energy as described above. In this way one can estimate also the best-fit ionization energies in the approximation of the theory applied. Probably the small errors in the closed subshell analytical expressions affect weakly the results of the computations of the observed astrophysical spectra and transition probabilities.

It is essential to specify reasonably a set for the initial values of parameters  $Z_{ni}^l$  in the radial Slater orbitals for the ground states of atoms and ions. A simple way is to use the ratio

$$E_{j,n}^l = \frac{E_H Z_j^2}{n_{\text{eff}}^2} \quad (86)$$

in order to estimate the effective quantum number of valence electrons  $n_e$ . Here  $E_{j,n}^l$  is the ionization energy of atom or ion  $j$ , having ionization stage  $Z_j$ . Replacing  $Z_j$  by its effective value, we obtain

$$Z_{ni}^l = \frac{Z_j}{n_{\text{eff}}} = \sqrt{\frac{E_{j,n}^l}{E_H}}. \quad (87)$$

For the low-excited states, corresponding to the principal quantum number  $n'$ , we accept for initialization a similar shift of effective principal quantum numbers

$$n'_{\text{eff}} = \frac{n'}{n} n_{\text{eff}}, \quad (88)$$

from where

$$Z_{n'i}^l = \frac{Z_j}{n'_{\text{eff}}} = \frac{n}{n'} \sqrt{\frac{E_{j,n}^l}{E_H}}. \quad (89)$$

These simple values for  $Z_{ni}^l$  can be used in software for the initialization of energy minimization computations. The screening of the nuclear electrostatic field grows outwards, and correspondingly the corrected values of the effective  $Z_{ni}^l/n$  in exponents must diminish. This generates a growing radial shift of nodes in the single configuration approximation in the consequential optimization procedure.

## 8. CONCLUDING REMARKS

In the present paper we have tried to give some contribution to the theory of complex atomic spectra. The analytical radial orbitals and the corresponding analytical Slater integrals for the solution of the Hartree–Fock equations by a variational method were proposed and studied by us many years ago (Sapar, 1973). Due to the lack of computing facilities we made no further efforts in this direction for decades, studying the stellar spectra and spectra of planetary nebula together with colleagues in the traditional ways, publishing even a collective monograph (Nikitin et al., 1986). Thereafter we published the Russian and later its English version of another collective monograph on spectra of planetary nebulae (Golovatyj et al., 1991, 1997).

Several years ago I started anew to discuss problems of analytical general formulae for astrospectroscopy. It is worth emphasizing that Rudzikas (2000), analysing in a review paper different self-consistent methods of the study of many-electron quantum systems, classified the method of analytical radial wave functions into the category of perspective ideas, forgotten by the mainstream investigators, preferring numerical computation of the Hartree–Fock–Jucys equations.

Finally, we try to summarize our main results of the present paper. These are:

- elaboration of an algorithm for the construction of the analytical orthonormal quasi-hydrogenic radial wave functions, including an analytical method of the solution of the system of these equations;
- deduction of analytical Slater integrals from the proposed Slater orbitals;
- elaboration of a general recurrent concept of diagonal Racah branching coefficients for the interaction of equivalent electrons for terms of unfilled subshells;
- presentation of general angular Racah branching fractions for the Hamiltonian of the binding energy of unfilled electron subshells;
- proposal to use the least squares method as a nonlinear optimization method in order to optimize the values of free parameters in the Hamiltonian by the Levenberg–Marquardt method of nonlinear optimization;
- proposal to specify the mixing coefficients in the Hamiltonian of multi-configurational interaction as automatically normalized direction cosines in the polar coordinate system of the  $n$ -dimensional Euclidian space.

To conclude, some general remarks. Using the radial integrals and perturbation theory, we also have derived analytical formulae for a specific mass shift, isotopic and hyperfine shift of spectral lines. The relativistic Breit–Pauli fine-structure splitting and the nuclear shifts are important, especially for large  $Z$  nuclei and high-stage ions, and mostly can be studied by perturbation theory. The Zeeman splitting inside spectral terms, generated by the nuclear magnetic field, can also be computed applying perturbation theory. The suggested proposals can help to avoid solving secular equations for best-fit energy values. The deduced analytical formulae enable also to carry out unified computations of the atomic electron transition probabilities. A drawback of the method is that the number of free parameters is large.

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## **Analüütilised valemid aatomi elektron-allkestade energiale ja nende optimeerimine**

Arved Sapor

Aatomite ja ioonide kirjeldamiseks on kasutusele võetud üldistatud analüütilised ortonormeeritud radiaalsed lainefunktsioonid, mis sisaldavad vabu parameetreid. Need optimeeritavad parameetrid määravad radiaalkaugusest sõltuva elektronide varjestatud tuumalaengu. Nende funktsioonide baasil on tuletatud analüütilised avaldised Slateri radiaalintegraalidele. Kasutades Racahi genealoogilisi koefitsiente, on tuletatud valemid ekvivalentsete elektronide hargnemisjaotusele spektritermide vahel erineva osalise täidetusega ekvivalentsete elektronide allkestades. Pauli keeluprintsiibist tulenevad piirangud on sel teel arvestatud ilmutamata kujul Racahi koefitsientide baasil, vältides keerukaid arvutusmeetodeid Clebschi-Gordani koefitsientide abil. Radiaalfunktsioonide vabade parameetrite optimeerimist hamiltoniaanil on otstarbekas teostada vähimruutude meetodi Levenbergi-Marquardti versioonil, kasutades lisatingimusena viriaali teoreemi kineetilise ja potentsiaalse energia suhte kohta. Seega on energia omaväärtuste määramine Hartree-Focki meetodil asendatud mittelineaarse optimeerimismeetodiga. Integraalid hamiltoniaanil vastavad elektronide kineetilisele energiale, elektronide elektrostaatilisele interaktsioonienergiale omavahel ja aatomituumaga. Viimane võtab arvesse kuloonilise ja vahetusmõju elektronpaaride vahel nende ühises allkestas või erinevates allkestades. Üleminekuks mitmekonfiguratsioonilisele lähendusmeetodile on soovitatud kasutusele võtta suunakoosinused  $n$ -dimensioonilise eukleidilise ruumi polaarkoordinaadistikus.