International Journal of Applied Engineering Research ISSN 0973-4562 Volume 12, Number 22 (2017) pp. 12961-12970
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Effective Integration Algorithm for Spin-Angular Variables for Many-Electron Atomic Systems

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Abstract

Studies of a wide array of processes leading to the excitation and ionization of many-electron atomic systems require the description of states with open electron shells. Existing calculation schemes for obtaining angular parts of the wave functions, operators matrix elements for spectroscopic and energy quantities are difficult in the case of complex electron configurations containing nonequivalent electrons, unfilled shells, especially of *d*- and *f*-symmetries. In this work we present an algorithm for constructing wave functions of arbitrary electronic configurations based on a combination of Slater's determinants approach and the technique of sequential coupling of orbital and spin moments on the basis of Clebsch-Gordan coefficients in the *LS*-coupling approximation. The possibility of applying the approach is demonstrated for the case of calculation of matrix elements of physical quantities for complex electron configurations on the example of the electric multipole transition operator. For the principal elements of the algorithm, their software implementation for a computer is presented. The efficiency of the proposed algorithm is illustrated by the example of calculating the angular structure of a complex configuration with four unfilled electron shells, as well as the wave functions of equivalent electrons of *s*-, *p*-, and *d* - symmetry.

Keywords: Many-Electron wave functions; Slater determinant; Clebsch-Gordan coefficients; orbital angular momentum; spin angular momentum; *3j*-symbol; coefficients of fractional parentage; *LS*-coupling.

INTRODUCTION

Modern atomic spectroscopy studies the structure and properties of practically any atom of the Mendeleyev's periodic table, and ions of any degree of ionization, including, in the processes of multiphoton absorption [1] and ionization [2], elastic [3] and inelastic [4] scattering of X-ray radiation, X-ray emission [5], cascade decay of deep inner-shells vacancies [6], etc. The Hartree-Fock method [7-10] is the basic theoretical method for interpreting the experimental data obtained in many applications of quantum chemistry, atomic spectroscopy and condensed state physics. At present, the solution of this method's the equations in the case of electron configurations with filled shells presents no difficulties. At the same time, obtaining angular parts of the wave functions of complex electron configurations remains, as before, the most difficult stage in the problem of description of vacancy states with open shells of various types of symmetry, and an accurate account of the electron correlations effects realized in such modifications of the Hartree-Fock method as the configurations interaction approximation [11], multiparticle perturbation theory [12], coupled clusters method [13], Hylleraas method [14], Monte Carlo method [15], etc.

The most common approaches to calculating angular parts of electron configurations wave functions are based on the use of tensor operators; they are founded on the classical papers by Racah [16-19]. In this case, it is assumed that not the angular parts of the wave functions themselves are obtained, but rather the expressions for the matrix elements of operators of physical quantities. The methods for calculation of a number of matrix elements [20-23] are based on the computational scheme proposed by Fano [24]. The idea of this scheme is based on the fact that the total wave function of an atom is constructed from antisymmetrized wave functions of individual shells with subsequent antisymmetrization of the total wave function of the system through the coefficients of fractional parentage [18]. Electron shells are coupled through their angular moments in the LS- or jj-coupling approximation. In this case, the calculation of matrix elements is reduced to the calculation of electrons-splitting-off matrices, and the coefficients of fractional parentage. With this approach, the calculation scheme is difficult to formalize and generalize, especially for configurations with nonequivalent electrons, and resulting recurrence relations are too laborious to perform calculations. A wide range of studies has been performed to overcome this situation. In particular, in the paper [25] two-particle coefficients of fractional parentage for the calculation of matrix elements was introduced. Nevertheless, this did not completely eliminate the above problems. Much later, in another paper [23] an approach that allowed the calculation of individual standard parts of the split-off matrices with coefficients of fractional parentage was presented. The program codes were developed [20-22,26,27]. The codes are meant for the calculation of the electron-split-off matrices. However, the calculation schemes used still remain laborious in calculations for electron configurations with open shells. In the paper [28], matrix elements were grouped into "classes" to simplify the

calculation procedure. Despite the promising of the idea, the approach wasn't widely used and wasn't even generalized for the case of all two-electron operators. In the papers [28,29] the authors used the technique of tensor operators that simplify calculations *via* reducing the matrix elements of unit tensors to a set of tabulated values, and the possibility to test non-zero spin-angular coefficients using selection rules. The calculation technique in this approach was developed only for diagonal matrix elements.

Outside the frame of coordinate representation [30-33] a quantization formalism whose advantage was in simplifying the form of the matrix elements of one- and two-particle operators of physical quantities was developed. Quite simple approaches were developed for some individual cases of three-particle operators [34]. These works made a significant contribution to the successful development of perturbation theory [12,35] and the orthogonal operators [36].

In addition to the tensor technique, the so-called direct diagonalization method has been developed [37]. It is based on the idea of representing the wave functions of electron configurations as a set of Slater determinants [38]. In this approach, calculation of the angular parts of wave functions is based on the calculation of matrix elements of the operators of the square of total orbital angular momentum $\hat{\boldsymbol{L}}^2$ and the square of total spin momentum $\hat{\boldsymbol{S}}^2$between Slater determinants, and subsequent simultaneous diagonalization of the two matrices of these operators [39-41]. This approach is better algorithmized, but the amount of computation is quite large and a special analysis is needed to reduce it to a required minimum. For example, for a four-shell configuration $ns^1mp^2nd^3mf^4$, the expansion contains 90328 determinants for the case of $M_L = 0$, $M_S = 0$, which requires impressive computational resources. This the principal drawback that hampers mass application of this method in practice.

To summarize, most of existing methods and computer codes used to find the angular coefficients of electron configurations wave functions encounter the following problems:

- a sufficiently large demand for computational resources for calculating the angular parts of matrix elements;
- limited applicability, *i.e.* possibility of obtaining angular structures only for relatively simple systems;
- complexity of algorithmization and general formalization of methods based on the classical Racah algebra, especially for cases of off-diagonal matrix elements of the Hamiltonian;
- limited possibility to include the configuration with open *d*- and *f*- shells in the calculation because of the complexity of the coefficients of fractional parentage for these cases.

In this paper, we propose an algorithm for calculating the angular parts of many-electron wave functions and matrix operators of physical quantities aimed at minimizing existing computational problems. The algorithm is based on a combination of approaches involving the representation of the wave function in the form of a set of Slater determinants and the use of a sequential independent coupling of spin and orbital angular momenta for an arbitrary electronic configuration based on the Clebsch-Gordan coefficients. A calculation scheme for off-diagonal matrix elements is proposed for the example of the electric multipole transition operator. For the principal elements of the algorithm, software implementations for a computer are presented. The effectiveness of the proposed algorithm is illustrated by the example of calculating the angular structure of a complex configuration with four unfilled electron shells and the wave functions of equivalent electrons of *s*-, *p*-, and *d*-symmetry.

THEORETICAL BACKGROUND

Mathematical basis of the algorithm

The mathematical basis of the algorithm is the representation of the many-electron wave function Φ(q), where $q = (q_1, q_2, \dots, q_N)$, as a linear combination of Slater determinants [38], in which one-electron orthonormal states (spin-orbitals) correspond to a certain electron configuration $n_1 {l_1}^{N_1} n_2 {l_2}^{N_2} \dots n_\delta {l_\delta}^{N_\delta}$, and $\sum_{i=1}^{\delta} N_i = N$. Here N_i is the number of electrons in the ith shell, and N is the total number of electrons; δ is a number of shell in the configurations:

$$\Phi(q) = \sum_k A_k \det\left|\alpha_1^k \dots \alpha_N^k\right\rangle. \tag{1}$$

The expansion coefficients fulfill the normalization condition

$$\sum_k |A_k|^2 = 1. \tag{2}$$

Slater determinants here and below have the form

$$\det|\alpha_1 \dots \alpha_N\rangle = \frac{1}{\sqrt{N!}} \sum_\lambda \varepsilon_\lambda \prod_{i=1}^{N} \psi_{\alpha\lambda i}(q_i)\,, \tag{3}$$

The summation is carried out over all permutations, $\varepsilon_\lambda = 1$ if the permutation λ is even, and $\varepsilon_\lambda = 1$ if it is odd. One-electron states are written as

$$\psi_\alpha(q) = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}(\sigma), \tag{4}$$

where $P_{nl}(r)$ is the radial part of the wave function obtained by the solution of Hartree-Fock equations or their modification, $Y_{lm_l}(\theta, \varphi)$is the angular part of one-electron wave function, $\chi_{m_s}(\sigma)$ is its spin part; n is a principal quantum number, l is an azimuthal quantum number, m_l is a magnetic quantum number, and $m_s = \pm 1/2$ is a quantum of spin projection.

Many-electron wave function must be an eigenstate of operators of the squared orbital and spin momenta, and he operators of their projections (onto z axis) [42],

$$\hat{\boldsymbol{L}}^2\Phi(q) = L(L+1)\Phi(q), \quad (5)$$

$$\hat{L}_z\Phi(q) = M_L\Phi(q), \quad (6)$$

$$\hat{\boldsymbol{S}}^2\Phi(q) = S(S+1)\Phi(q), \quad (7)$$

$$\hat{S}_z\Phi(q) = M_S\Phi(q), \quad (8)$$

In addition, it must be asymmetric and have a certain parity P.

The basic idea underlying the procedure for constructing the many-electron wave function within the proposed approach is the independence of the operations of binding the electrons' moments and antisymmetrization of the function itself; it reduces to the following general Algorithm 1.

Algorithm 1. Construction of many-electron system's wave functions.

Algorithm 1.Construction of many-electron system's wave functions

Step1: Selection of states $\{\alpha_1^k \dots \alpha_N^k\}$characterized by$M_L$ and M_S

Step2: Determination of the order of coupling of orbital and spin moments.

Step3: Determination of the expansion coefficientsA_k

Selection of states $\{\alpha_1^k \dots \alpha_N^k\}$ characterized by M_L and M_S

Selection of the states entering (1) is performed by the quantum numbers $M_L$and M_S. The operators $\hat{L}_z$ and $\hat{S}_z$ commute with the Hamiltonian [43], but here it is not necessary to build and diagonalize corresponding matrices, as in the case of the operators $\hat{\boldsymbol{L}}^2$and $\hat{\boldsymbol{S}}^2$.

The following relation holds for the operator $\hat{L}_z$ and an arbitrary determinant (3), [42]:

$$\hat{L}_z\det|\alpha_1 \dots \alpha_N\rangle = \left(\sum_{i=1}^{N} m_{l_i}\right)\det|\alpha_1 \dots \alpha_N\rangle, \quad (9)$$

Therefore, only those states for which the $\sum_{i=1}^{N} m_{l_i} = M_L$ enter the expansion (1).

Analogous relation holds for the operator $\hat{S}_z$ [43]:

$$\hat{S}_z\det|\alpha_1 \dots \alpha_N\rangle = \left(\sum_{i=1}^{N} m_{s_i}\right)\det|\alpha_1 \dots \alpha_N\rangle, \quad (10)$$

The expansion (1) includes states for which the $\sum_{i=1}^{N} m_{s_i} = M_S$.

If the configuration contains equivalent electrons in one shell $n_k {l_k}^{N_k}$, a verification of the fulfillment of the Pauli principle is necessary.If same-*l* equivalent electrons in a selected state have the same quantum numbers m_{l_i} and m_{s_i} than such state is rejected as physically non-existent.

Thus, of all possible combinations of single-electron states $\{\alpha_j\}$ of a given configuration, the sum (1) will contain only those Slater determinants that satisfy the above conditions.

Determination of the order of coupling of orbital and spin moments

The antisymmetric wave functions of equivalent electrons can be built only for cases of *LS*- and *jj*-coupling [42]. Since for most elements of the periodic table *LS*-coupling is prevailing further consideration is based on this coupling scheme. For equivalent electrons, a definite order of orbital and spin moments coupling cannot be established. The resulting term αLS(α distinguishes same – *LS* terms) of the wave function of equivalent electrons is determined by the set of parent terms of the wave function of *N*-1 equivalent electrons. Sets of parent terms for individual electron shells of *s*-, *p*-, *d*- and *f*-symmetries are defined in [29].

For the wave function of a complex electron configuration, the algorithm realizes the sequential coupling of orbital and spin moments of individual shells of equivalent electrons. The following scheme corresponds to the procedure of coupling:

$$n_1{l_1}^{N_1}(L_1S_1)\otimes n_2{l_2}^{N_2}(L_2S_2)\ [L_{12}S_{12}]\otimes n_3{l_3}^{N_3}(L_3S_3)[L_{123}S_{123}] \dots \otimes n_u{l_u}^{N_u}(L_uS_u)\ LS.$$

Determination of the expansion coefficients A_k for the wave functions of equivalent electrons

For the wave function of the electron shell $l^N(\alpha LSM_LM_S)$ built according to (1), the calculation of the expansion coefficients A_k satisfying condition (2) is performed on the basis of the procedure for selecting the states and the procedure for binding the orbital and spin moments.

The coefficients A_k are calculated on the basis of the recurrence relations presented by Algorithm 2.When writing Algorithm 2, we use notations and computational details, a complete list of which is presented in Appendix A.

In the sketch of Algorithm 2 above there is a fragment of the code illustrating the procedure for calculating the expansion coefficients A_k for the of the wave function of an arbitrary electron shell $l^N(\alpha LSM_LM_S)$. The algorithm is based on sequential coupling of orbital and spin moments of all electrons in the l^N shell for a given αLSM_LM_S term.

Algorithm 2: The construction of wave functions of equivalent electrons.

1. **subroutine** CalculAngularStructureWaveFunctionsEE
2. ***for*** k=1 *to* N_{State}
3. $A_1(TM|\{m\}_k)$ =1
4. ***for*** NN=2 *to N*
5. *AS=0*
6. ***for*** t=1 *to* N_{term}
7. *BS=0*
8. ***for*** β=1 *to N*
9. $BS=BS+A_{NN-1}\left(\theta_t M_\beta \middle| \{m_\beta\}_k\right)\cdot \left[L_t\ l\ M_{L\beta} m_{l\beta} \middle| L\ M_L\right]\cdot\left[S_t\ s\ M_{S\beta} m_{s\beta} \middle| S\ M_S\right]$
10. ***end***
11. $B_{NN}(\theta_t M|\{m\}_k) = BS$
12. $AS=AS+B_{NN}(\theta_t M|\{m\}_k)$
13. ***end***
14. $A_{NN}(TM|\{m\}_k)$ =*AS*
15. ***end***
16. ***end***
17. SS=0
18. ***for*** k=1 *to* N_{State}
19. $SS=SS+A_N(TM|\{m\}_k)^2$
20. ***end***
21. $A_N(TM|\{m\}_k) = A_N(TM|\{m\}_k)/\sqrt{SS}$
22. **endsubroutine**

The loop for the variable k runs through the decomposition states (1), the number of which is defined as N_{State}. For each state $\{m\}_k$ of the k-th electron shell the required coefficient $A_N(TM|\{m\}_k)$ is calculated based on the recurrence relations presented in lines 3, 12, and14 of Algorithm 2. The main element of the algorithm is the cycle (see lines 6-10 of Algorithm 2) for the calculation of $B_{NN}(\theta_t M|\{m\}_k)$. In this recurrent expression, the orbital and spin moments of the electron NN are coupled to the electrons of $l^{N-1}(\alpha_k L_k S_k)$ using Clebsch-Gordan coefficients [44]: $\left[\mathrm{L_t\ l\ M_{L\beta} m_{l\beta}} \middle| \mathrm{L\ M_L}\right]$ and $\left[\mathrm{S_t\ s\ M_{S\beta} m_{s\beta}} \middle| \mathrm{S\ M_S}\right]$(see line 9 of Algorithm 2). At the final stage, in lines 19-21 of Algorithm 2, the normalization of the resulting wave function is performed in accordance with (2).

This algorithm is universal and can be applied to electron shells of any symmetry and occupancy.

Determination of the expansion coefficients $\mathrm{A_k}$ for the wave functions of complex configurations

Calculation of the expansion coefficients $\mathrm{A_k}$ for the wave function of a complex electron configuration $n_1 l_1^{N_1}(\alpha_1 L_1 S_1)\ldots. n_\delta l_\delta^{N_\delta}\left(\alpha A_{k_\delta} L_\delta S_\delta\right) LSM_L M_S$ build in accordance with (1) and satisfying the condition (2) is performed on the basis of the procedure for selecting states and the procedure for coupling orbital and spin moments.

The algorithm for the calculation of A_k for complex configurations is similar to Algorithm 2 in the part of the implementation of the procedure for coupling the electron moments. In this case, the coupling of moments of an individual electron shell is performed. We suppose that within each shell, the LS-coupling scheme is realized. The state of each electron shell is characterized by the resultant term $\alpha_i L_i S_i$, where$i = 1,2,..,u$, and u denotes the number of shells in the configuration

Algorithm 3: The construction of wave functions of many-electron systems.

1. **subroutine**CalculAngleStructureFunction
2. ***for*** k=1 *to* N_{State}
3. CP =1
4. ***for*** is=1 *to u-1*
5. $CP=CP\cdot\left[L_{[is]}L_{is+1}M_{L_{[is]}}M_{L_{is+1}} \middle| L_{[is+1]}M_{L_{[is+1]}}\right]$
6. $CP=CP\cdot\left[S_{[is]}S_{is+1}M_{S_{[is]}}M_{S_{is+1}} \middle| S_{[is+1]}M_{S_{[is+1]}}\right]$
7. ***end***
8. AP =1
9. ***for*** is=1 *to u*
10. $AP=AP\cdot A_{nl}(T_{is}M_{is}|\{m_{is}\}_k)$
11. ***end***
12. $A(TM|\{m\}_k) = AP\cdot CP$
13. ***end***
14. SS=0
15. ***for*** k=1 *to* N_{State}
16. $SS=SS+A(TM|\{m\}_k)^2$
17. ***end***
18. $A(TM|\{m\}_k) = A(TM|\{m\}_k)/\sqrt{SS}$
20. **endsubroutine**

When writing Algorithm 3, we use notations and computational details, a complete list of which is presented in Appendix A.

The above Algorithm 3 is a fragment of the code illustrating the procedure for calculating the expansion coefficients A_k of the wave function of an arbitrary complex electron configuration. The algorithm is based on the sequential coupling of orbital and spin moments of the electron shells $n_j l_j^{N_j}$ with a given term $\alpha_i L_i S_i$.

A cycle with variable k runs through the decomposition states (1); their number denoted as asN_{State}. For each state of the k-th electron configuration $\{m\}_k$a sequential coupling of orbital moments (line 5 of Algorithm 3) and the spin moments (line 6 of Algorithm 3) of the electron shells entering the configuration *via*Clebsch-Gordan coefficients $\left[L_{[is]}L_{is+1}M_{L_{[is]}}M_{L_{is+1}}\middle| L_{[is+1]}M_{L_{[is+1]}}\right]$ and $\left[S_{[is]}S_{is+1}M_{S_{[is]}}M_{S_{is+1}}\middle| S_{[is+1]}M_{S_{[is+1]}}\right]$ [42] is performed (lines 3-7 Algorithm 3). The electron shells themselves contribute to the coefficient A_k, in particular, their states being couples. Taking into account the contributions of the shells is given in lines 8-11 of Algorithm 3.

At the final stage, in lines 19-21 Algorithm 3, in accordance with (2), the normalization of the coefficients of the wave function obtained is performed.

The fragment of the code presented in Algorithm 3 allows obtaining the structure of wave functions with any number of unfilled shells without increasing the requirements for computational resources.

Computational scheme for matrix elements of spectroscopic quantities

Representation of the wave functions of the electron configurations in the form (1) allows one to efficiently algorithmize the calculation of matrix elements the operators of spectroscopic quantities using the expressions first obtained by Löwdin [44].

We shall carry out the implementation of the algorithm using the example of calculating the matrix element of the electric multipole transition operator. Following refs. [45, 46], the expression for the matrix element of the electric multipole transition operator between two arbitrary determinants can be represented in the form

$$\langle Det_a|\hat{Q}|Det_b\rangle = \sum_{i,j=1}^{N} \langle\psi_{a_i}|Q^{(k)}\left|\psi_{b_j}\right\rangle D_{ab}(\psi_{a_i}\psi_{b_j}), \quad (11)$$

where $D_{ab}\left(\psi_{a_i}\psi_{b_j}\right)$ is the algebraic complement to the overlap integral of the wave functions $\left\langle\psi_{a_i}\middle|\psi_{b_j}\right\rangle$ in the determinant D_{ab}, that is, it is a minor with its sign $(-1)^{i+j}$, obtained from the matrix $||D_{ab}||$ by deleting the i-th row and the j-th column.

The computational problem reduces to the calculation of the matrix element $\left\langle\psi_{a_i}\middle|Q^{(k)}\middle|\psi_{b_j}\right\rangle$. According to the Wigner-Eckart theorem, this expression can be factorized into the angular and radial parts [29], namely

$$\langle nlm_l|Q_q^{(k)}|n'l'm'_l\rangle = \langle nl|r^k|n'l'\rangle\left(l|C^{(k)}\middle|l'\right)[l'\,km'_l q|lm_l], \quad (12)$$

where$\langle nl|r^k|n'l'\rangle$ is the radial part of the multipole transition, and $\left(l|C^{(k)}\middle|l'\right)$is the matrix element of the spherical harmonic.

Expressions (11) and (12) form the basis of Algorithm 4 for calculating the matrix elements of the electric multipole transition operator. This approach can be extended to any one- and two-particle operators.

The above Algorithm 4 shows a fragment of the code illustrating the procedure for calculating matrix element of the multipole transition operator. Embedded loops with operator brackets represented in lines 3, 4 and 14, 15, perform running over the states k and g of the wave functions of electron configurations in the left and right parts of the operator. For each state composition (k, g), the matrix element is calculated in accordance with (11) (see lines 6-12 of Algorithm 4). The algorithm can be extended to calculate diagonal and off-diagonal matrix elements for arbitrary electronic configurations.

Algorithm 4: Calculation of the matrix element of the transition operator multipole.

```
1.  subroutineCalculMPTransition
2.    ME=0
3.    for k=1 to NX_State
4.      for g=1 to NY_State
5.        MES =0
6.      forisx=1 to N
7.          forisy=1 to N
8.            QME=⟨nlm_l|Q_q^(k)|n'l'm'_l⟩
9.            RIntOrt=D_ab(nlm_l, n'l'm'_l)
10.             MES=MES+RIntOrt · QME
11.         end
12.       end
13.       ME=ME+A_a(k) · A_b(g) ·MES
14.     end
15.   end
16.   endsubroutine
```

When writing Algorithm 4, we use notations and computational details, a complete list of which is presented in Appendix A.

RESULTS AND DISCUSSIONS

As an example, consider two-electron wave functions of s-, p- and d-symmetry. To simplify the form of equations, we introduce the following notation: a positive projection of the spin moment onto z axis will be denoted as "+", and negative as "-"; the projections of the orbital angular momentum (magnetic quantum numbers) will be represented by numbers. For example, for two equivalent d-electrons in the states with $m_{l_1} = 2, m_{s_1} = 1/2$and $m_{l_2} = 1, m_{s_2} = -1/2$, the state of the wave function electrons is written as $|2^+, 1^-\rangle$.

Two-electron wave functions of s symmetry. Consider two s-electrons, each being in the state ^2S $(L = 0, S = 1/2)$. Coupling of orbital and spin moments brings the two-electron system to the state ^1S $(L = 0, S = 0)$, while the only possible projections of the moments are $M_L = 0, M_S = 0$ (see Sect. 2.3). Such a system can exist only in one state, $|0^+, 0^-\rangle$. According to Algorithm 2, the only expansion coefficient is $A_1(0^+, 0^-) = 1$. The two-electron wave function then has the form $\Psi(s^2,\ ^1\boldsymbol{S}, M_L = 0, M_S = 0) = |0^+, 0^-\rangle$.

Two-electron wave functions of p symmetry. Consider two p-electrons, each being in the state ^2P $(L = 1, S = 1/2)$. After coupling of orbital and spin moments, the two-electron system can be found in one of three states: ^1S, ^1D, ^3P[44].

Let us first build a two-electron wave function for the term ^1S. In this case, the only possible projections of the moments are $M_L = 0, M_S = 0$. Obviously, three possible states correspond to this electron configuration (see Sect. 2.2), namely

$$|1^+, -1^-\rangle_{[1]}, |0^+, 0^-\rangle_{[2]}, |1^-, -1^+\rangle_{[3]} \tag{13}$$

In accordance with Algorithm 2, the coefficients of coupled states have the form

$$A_1(1^+, -1^-) = \sqrt{2}[1\ 1\ 1 - 1|0\ 0] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle| 00\right] = \frac{1}{\sqrt{3}} \tag{14}$$

$$A_2(0^+, 0^-) = \sqrt{2}[1\ 1\ \ 0\ \ 0|\ 0\ 0] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle| \frac{1}{2}0\right] = -\frac{1}{\sqrt{3}} \tag{15}$$

$$A_3(1^-, -1^+) = \sqrt{2}[1\ 1\ \ 1\ \ -1|\ 0\ 0] \cdot \left[\frac{1}{2}\frac{1}{2} - \frac{1}{2}\frac{1}{2}\middle| 0\ 0\right] = -\frac{1}{\sqrt{3}} \tag{16}$$

The common factor in the coefficients is due to the normalization condition (2). Thus, the wave function has the form:

$$\Psi(p^2,\ ^1\boldsymbol{S}, M_L = 0, M_S = 0) = \frac{1}{\sqrt{3}}|1^+, -1^-\rangle_{[1]} - \frac{1}{\sqrt{3}}|0^+, 0^-\rangle_{[2]} - \frac{1}{\sqrt{3}}|1^-, -1^+\rangle_{[3]} \tag{17}$$

For the term ^3P, coupling of electron moments for states (13) gives the following expressions

$$A_1(1^+, -1^-) = \sqrt{2}[1\ 1\ 1 - 1|1\ 0] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle| 1\ 0\right] = \frac{1}{\sqrt{2}} \tag{18}$$

$$A_2(0^+, 0^-) = \sqrt{2}[1\ 1\ \ 0\ \ 0|0\ 0] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle| 10\right] = 0 \tag{19}$$

$$A_3(1^-, -1^+) = \sqrt{2}[1\ 1\ \ 1\ \ -1|1\ 0] \cdot \left[\frac{1}{2}\frac{1}{2} - \frac{1}{2}\frac{1}{2}\middle| 0\ 0\right] = \frac{1}{\sqrt{2}} \tag{20}$$

Thus, we obtain a two-electron wave function for the term ^3P in the form

$$\Psi(p^2,\ ^3\boldsymbol{P}, M_L = 0, M_S = 0) = \frac{1}{\sqrt{3}}|1^+, -1^-\rangle_{[1]} + \frac{1}{\sqrt{3}}|1^-, -1^+\rangle_{[3]} \tag{21}$$

Two-electron wave functions of d symmetry. Consider two d-electrons, each being in the state ^2D $(L = 2, S = 1/2)$. After coupling orbital and spin moments, the two-electron system can be in one of the following states: ^1S, ^1D, ^3P, ^1G, ^3F [44]. For example, let us build a two-electron wave function with the term ^3F.

Consider the case when the projections of the moments are $ML = 1$, $MS = 1$. In this case, two possible states correspond to the electron configuration, namely

$$|2^+, -1^-\rangle_{[1]}, |1^+, 0^+\rangle_{[2]} \tag{22}$$

The coefficients obtained as a result of the execution of Algorithm 2 have the form

$$A_1(2^+, -1^-) = \sqrt{2}[2\ 2\ 2 - 1|3\ 1] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\middle|\ 1\ 1\right] = \sqrt{\frac{3}{5}} \tag{23}$$

$$A_2(1^+, 0^+) = \sqrt{2}[2\ 2\ \ 1\ \ 0|3\ 1] \cdot \left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\middle| 1\ 1\right] = \sqrt{\frac{2}{5}} \tag{24}$$

Thus, we obtain a two-electron wave function for the term ^3F in the form:

$$\Psi\left(d^2,\ {}^{\mathbf{3}}\boldsymbol{F}, M_L = 1, M_S = 1\right) = \frac{1}{\sqrt{5}}\left(\sqrt{3}\left|2^+, -1^-\right\rangle_{[1]} + \sqrt{2}\left|1^+, 0^+\right\rangle_{[2]}\right) \quad (25)$$

Many-electron wave function. Let us consider an example of calculating the expansion coefficients of the wave function for a complex electron configuration $n_1s^1(\,^2S)n_2s^1(\,^2S)[\,^{\mathbf{1}}\boldsymbol{S}]n_3p^1(\,^2P)[\,^{\mathbf{1}}\boldsymbol{P}]n_4s^1(\,^2S),\ {}^{\mathbf{1}}\boldsymbol{P}, M_L = 0, M_S = 0$. According to the established rules for the selection of states (see Sect. 2.2.), this configuration has 4 states, namely

$$\left|0^+,0^-,0^+,0^-\right\rangle_{[1]},\ \left|\left|0^+,0^-,0^-,0^+\right\rangle_{[2]}, \left|\left|0^-,0^+,0^+,0^-\right\rangle_{[3]}, \left|\left|0^-,0^+,0^-,\right.\right.\right. \quad (26)$$

We find the coefficients of the bound states of the basis following Algorithm 3. Since each shell contains one electron, the expansion coefficient is completely determined during the coupling of electron moments without the need to calculate the coefficients of the wave functions of equivalent electrons via Algorithm 2. Coupling of orbital and spin moments is performed independently and leads to the following expressions:

$$\mathrm{C}_L = [0\ 0\ 0\ 0|0\ 0]\cdot[0\ 1\ 0\ 0|1\ 0]\cdot[1\ 0\ 0\ 0|1\ 0] = 1 \quad (27)$$

$$A_1(0^+,0^-,0^+,0^-) = \mathrm{C}_L\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle|00\right]\cdot\left[0\frac{1}{2}0\ \ \frac{1}{2}\middle|\frac{1}{2}\frac{1}{2}\right]\cdot\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle|00\right] = \frac{1}{2} \quad (28)$$

$$A_2(0^+,0^-,0^-,0^+) = \mathrm{C}_L\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle|00\right]\cdot\left[0\frac{1}{2}0\ -\frac{1}{2}\middle|\frac{1}{2}\ -\frac{1}{2}\right]\cdot\left[\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\frac{1}{2}\middle|00\right] = -\frac{1}{2} \quad (29)$$

$$A_3(0^-,0^+,0^+,0^-) = \mathrm{C}_L\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\middle|00\right]\cdot\left[0\frac{1}{2}0\ \frac{1}{2}\middle|\frac{1}{2}\frac{1}{2}\right]\cdot\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\middle|00\right] = -\frac{1}{2} \quad (30)$$

$$A_4(0^-,0^+,0^-,0^+) = \mathrm{C}_L\left[\frac{1}{2}\frac{1}{2}\ -\frac{1}{2}\frac{1}{2}\middle|00\right]\cdot\left[0\frac{1}{2}0-\frac{1}{2}\middle|\frac{1}{2}-\frac{1}{2}\right]\cdot\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}\middle|00\right] = \frac{1}{2} \quad (31)$$

Thus, the structure of the wave function of a complex configuration in this case is

$$\Psi\left(n_1s^1(\,^2S)n_2s^1(\,^2S)[\,^{\mathbf{1}}\boldsymbol{S}]n_3p^1(\,^2P)[\,^{\mathbf{1}}\boldsymbol{P}]n_4s^1(\,^2S),\ {}^{\mathbf{1}}\boldsymbol{P}, M_L = 0, M_S = 0\right) = \frac{1}{2}\left(\left|\left|0^+,0^-,0^+,0^-\right\rangle_{[1]} - \left|\left|0^+,0^-,0^-,0^+\right\rangle_{[2]} - \left|\left|0^-,0^+,0^+,0^-\right\rangle_{[3]} + \left|\left|0^-,0^+,0^-,0^+\right\rangle_{[4]}\right.\right.\right.\right. \quad (32)$$

The presented results show the effectiveness of the developed algorithm, both for wave functions of equivalent electrons, and for complex configurations. The results of the calculation are in agreement with the data obtained earlier in [38, 39, 42].

CONCLUSIONS

The algorithm for calculating the angular parts of many-electron wave functions presented in this paper is based on the expansion of the wave function in Slater determinants. The realized technique of coupling orbital and spin electron moments on the basis of the Clebsch-Gordan coefficients in the *LS*-coupling approximation shows its effectiveness in application to arbitrary electronic configurations. The approach used is free from existing drawbacks of the technique of fractional parentage coefficients and split-off matrices, as well as from the need to diagonalize large-dimensional matrices. This approach makes it possible to calculate diagonal and off-diagonal matrix elements of spectroscopic operators. The algorithm is low-cost from a computational point of view. Considered examples of building the wave functions are completely consistent with the existing results.

ACKNOWLEDGMENTS

This work is supported by the Grant of the President of Russian Federation No. 14.W01.17.2210-MK of 22.02.2017.

AUTHOR CONTRIBUTIONS

Anton Kasprzhitskii is responsible for the testing, validation and development of the algorithm for the construction of wave functions of many-electron systems and calculation of the matrix element of the transition operator multipole. GeorgyLazorenko is responsible for the testing, validation and development of the algorithm for the construction of wave functions of equivalent electrons. The initial concept of the algorithm was proposed by Victor Yavna. All of the authors contributed for the publication of this manuscript.

APPENDIXA

Notation list

Notation	Meaning
$T \equiv \alpha LS$	The term is an abbreviated description of the orbital (L) and spin (S) angular momentum quantum numbers in a many-electron atom. The α distinguishes same – LS terms.
$\theta_k \equiv \alpha_k L_k S_k$	The k-th parental term of the wave function of N-1 equivalent electrons generates the αLS - term of the wave function of N equivalent electrons
L_i	Orbital moment of the *i*-th electron shell
M_{L_i}	Projection of the orbital moment of the *i*-th electron shell
S_i	Spin moment of the *i*-th electron shell
M_{S_i}	Projection of the spin moment of the *i*-th electron shell
$L_{[n]}$	Total orbital momentum *n* of electron shells
$M_{L_{[n]}}$	Projection of total orbital momentum *n* of electron shells
$S_{[n]}$	Total spin momentum *n* of electron shells
$M_{S_{[n]}}$	Projection of total spin momentum n of the electron shells
$M \equiv (M_L, M_S)$	Projection of total orbital and spin moments
$M_i \equiv (M_{L_i}, M_{S_i})$	Projection of total orbital and spin moments of the *i*-th state
$M_{L\beta} = \sum_{i=1, i\neq\beta}^{N} m_{l_i}$	Sum of the projections of orbital moments of the electrons, except for the β-th electron
$M_{S\beta} = \sum_{i=1, i\neq\beta}^{N} m_{s_i}$	Sum of the projections of the spin moments of the electrons, except for the β-th electron
$M_\beta \equiv (M_{L\beta}, M_{S\beta})$	Projection of total orbital and spin moments, except for the β-th electron
$[l_1 l_2 m_1\ m_2 \mid L\ M]$	Clebsch-Gordan coefficient coupling the orbital moments l_1 and l_2 with the projections $m_1$and m_2, respectively, obtaining the function with the orbital moment L and the projection M. Calculation of Clebsch-Gordan coefficients can be performed by the following [44]
$\left(l \middle\| C^{(k)} \middle\| l'\right)$	Matrix element of the *k*-thspherical harmonic. Calculation of matrix element of the spherical harmonic can be performed by the following [44]
$m_i \equiv (m_{l_i}, m_{s_i})$	Projections of orbital and spin moments of the *i*-th electron
$\{m\}_k$	Set of m_i values for all electrons of the *k*-th state.
$\{m_\beta\}_k$	Set of m_i values for all electrons of the *k*-th state, except for the β-th electron

$A_a(k)$	Expansion coefficient of the *k*-th state of the many-electron wave function in (1).
$D_{ab}(nlm_l, n'l'm'_l)$	Algebraic complement to the overlap integral of the wave functions $\left\langle \psi_{nlm_{l_i}} \middle\vert \psi_{n'l'm'_l} \right\rangle$ in the determinant D_{ab}. Calculation of Algebraic complement can be performed by the following [45].

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