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Calculation of atomic integrals using commutation relations

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In this paper, a numerically stable method of calculating atomic integrals is suggested. The commutation relations among the components of the angular momentum and the Runge-Lenz vector are used to deduce recurrence relations for the Sturmian radial functions. The radial part of the one- and two-electron integrals is evaluated by means of these recurrence relations. The product of two radial functions is written as a linear combination of the radial functions. This enables us to write the integrals over four radial functions as a linear combination of the integrals over two radial functions. The recurrence relations for the functions are used to derive the recursion relations for the coefficients of the linear combination and for the integrals over two functions.

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I. INTRODUCTION

This paper is concerned with the calculation of atomic wave functions and atomic integrals in an algebraic way. This algebraic approach compares favorably with the analytical one. The algebraic approach enables us to handle the numerical instabilities encountered when calculating atomic integrals. There is also an inherent elegance in this approach.

The accuracy of the spectroscopic measurements achieved such a level that parity violating effects of the weak interactions on the atomic spectra can be measured. For a review of these exciting developments see, e.g., Refs. [1,2]. Together with the corresponding theoretical calculations, see, e.g., Ref. [3], this provides bounds on the mass of new neutral bosons predicted by extensions of the standard model. These bounds are tighter than those achieved in the present collider experiments [3]. Undoubtedly, the search for effects of the physics beyond the standard model on the atomic spectra will continue. More accurate measurements and calculations will be made. In this connection we would like to draw attention to the fact that there is an obstacle in further improvement of the theoretical calculations.

Let us restrict our discussion to the cases when the motion of electrons can be treated in the first approximation as nonrelativistic. Only slight modifications of the following discussion are needed to treat the cases when relativity has to be taken into account from the very beginning. The most accurate approximate method for solution of the Schrödinger equation for many-electron atoms is the method of configuration interaction (CI). It consists of expanding the exact wave function into the antisymmetrized products of one-electron spin orbitals. The orbital component of the spin orbitals is the product of the radial and angular parts.

The CI method can be systematically improved by enlarging the set of one-electron spin orbitals. However, in doing so the following difficulty is encountered. If we consider the orthogonal set of one-electron spin orbitals, we have to include the spin orbitals with radial functions having large number of nodes into the set. These functions change their sign frequently. Calculation of the matrix elements of the Coulomb interaction between these functions in finite precision arithmetics corresponds, from numerical point of view, to the subtraction of two infinities. If we consider nonorthogonal basis set, then we just shift the problem of numerical instabilities from the calculation of the integrals to the diagonalization of Hamiltonian matrix. So far the numerical instabilities have not been analyzed in a systematic way. Thus, they are not controlled. The difficulty caused by numerical instabilities is evident when observing the published numerical calculations.

The form of one-electron spin orbitals is in principle arbitrary. However, to achieve rapid convergence of the CI method, the Sturmian basis set is usually applied, see, e.g., Refs. [4–8]. This set is obtained from hydrogenic basis set via energy-dependent scaling transformation. The solution of the Schrödinger equation for the hydrogen atom is found to be a product of radial and angular functions. The difference in dealing with radial and angular functions is striking. The angular functions are found from commutation relations of so(3) algebra. This enables one to transform the angular integrations of complicated expressions to manageable algebraic manipulations [9–11]. On the other hand, the radial functions are not found from symmetry considerations but as solutions of differential equation. However, this leads to much less manageable numerical instabilities in the radial part of the integration mentioned above.

This observation is the chief motivation for the search of the algebraic treatment of the radial functions presented in this paper. This algebraic treatment is facilitated by high symmetry of the hydrogen atom. There are six operators commuting with hydrogenic Hamiltonian when neglecting spin. They consist of components of angular momentum and components of the Runge-Lenz vector. This vector is integral of motion also in the classical theory. This is a direct consequence of the fact that the classical orbit in Coulomb potential is a conic section. The Runge-Lenz vector has the direction of the principal axis of the conic section. Its magnitude equals to the eccentricity of the conic section, see, e.g., Ref. [12]. These six operators do not mutually commute. However, they are closed under commutation and form so(4) algebra. In addition, there are three radial operators closed under commutation that form so(2,1) algebra. After the energy-dependent scaling transformation so(4) algebra can be merged with so(2,1) algebra into so(4,2) algebra, see, e.g., Ref. [13].

The commutation of the Runge-Lenz vector with hydrogenic Hamiltonian was realized by Pauli even before the discovery of the Schrödinger equation. It was further elaborated by Fock and Bargmann (for an English translation of the original papers see Ref. [14]). Despite the fact that this high symmetry of the hydrogen atom has been known for such a long time it was seldom applied to more complicated atoms. Particularly, Herrick and Sinanoglu applied it to the classification of the doubly excited states of two-electron atoms [15]. Further, de Prunele applied it to the evaluation of the matrix elements of Coulomb interaction in the basis used by Herrick and Sinanoglu [16].

The first aim of this paper is to explore the high symmetry of the hydrogen atom and to relate it to the properties of radial functions. So far, only partial symmetry has been utilized via so(2,1) algebra of radial operators [13,17]. This provided the recurrence relations for radial functions with different principal number n but with the same orbital number l. The ultimate goal is to examine if so(4) algebra relates radial functions with different orbital numbers l. The second aim of this paper is to show that these relations for the radial functions can be used to numerically stabilize the calculation of the matrix elements of Coulomb interaction.

The paper is organized as follows. In Sec. II the energy spectrum of the hydrogen atom and the recurrence relations connecting the radial functions of the hydrogen atom with the same principal number n but different orbital number l are deduced. In Sec. III we consider so(2,1) algebra of radial operators. We make the energy-dependent scaling to transform the set of hydrogen basis functions pertaining to the discrete part of the spectrum to the Sturmian basis set. It is shown that the existence of so(2,1) algebra implies recurrence relations connecting the radial functions with the same orbital number l but different principal number n. Finally, these relations are combined with the ones derived in Sec. II to deduce the relations that are advantageous for further calculations. The rest of the paper is devoted to the applications of these recurrence relations. In Sec. IV the calculation of the matrix elements of Coulomb interaction is described in detail. First, the multipole expansion of the Coulomb potential is used to separate the radial and angular degrees of freedom. Further, the product of two radial functions is written as a linear combination of the radial functions. Numerically stable recurrence relations for the coefficients of the linear combination are derived. The linearization of the product of radial functions is used to write the integrals over four radial functions as the linear combination of the integrals over two radial functions. From recurrence relations for the radial functions, the recurrence relations for the reduced integrals are derived. This section constitutes a major development of the computation of the radial integrals. In Sec. V the method developed in this paper is used for CI calculation of the $1\,^1S$, $2\,^3S$, and $2\,^3S$ states of helium. In Appendix A the algebra of the angular operators is studied and the action of the angular operators on the angular functions is determined. This appendix summarizes the results concerning the so(3) vector operators necessary for the purposes of this paper. Finally, in Appendix B the one-electron integrals needed in Sec. IV are calculated.

To make the paper understandable for wide audience we completely avoid all the nomenclature of the mathematical theory of Lie algebras. To understand this paper it is sufficient to know the basic notions of quantum mechanics such as commutator, eigenvectors, and eigenvalues. The atomic units and Einstein summation convention will be used throughout this paper.

II. HYDROGEN ATOM

In this section the algebraic solution of hydrogen atom is given. It is shown that the Runge-Lenz vector commutes with the Hamiltonian of the hydrogen atom and it is a special case of so(3) vector operator. The matrix elements of so(3) vector operators between spherical harmonics yield the energy spectrum and the recurrence relations for the radial functions of the hydrogen atom. These recurrence relations connect the radial functions with the same principal number n but different orbital numbers l. The matrix elements of so(3) vector operators between spherical harmonics needed in this section are derived in Appendix A.

A. Energy spectrum of the hydrogen atom

Let us consider the problem of the nonrelativistic hydrogen atom

$$H|n,l,m\rangle = -\frac{1}{2n^2}|n,l,m\rangle, \tag{1}$$

where the Hamiltonian is given by

$$H = -\frac{\nabla^2}{2} - \frac{1}{r}. \tag{2}$$

At this point we assume that n is a positive real number. Later on we show that n has to be a positive integer.

Because of the spherical symmetry of the problem, it is advantageous to make the transition between Cartesian and spherical coordinates

$$x_k = rn_k. \tag{3}$$

Here, r is the radial distance and n_k are components of the corresponding unit vector

$$\vec{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta). \tag{4}$$

Indices j, k and so on, range from 1 to 3. The letter i is reserved for the square-root of minus one.

Using the chain rule for the differentiation of composed functions, expression of the operator ∇_k in terms of the variables r, θ, and φ reads

$$\nabla_k = \frac{\partial}{\partial x_k} = n_k\frac{\partial}{\partial r} + \frac{\nabla_k^n}{r}. \tag{5}$$

Here, the angular differential operator ∇^n was introduced by

$$\nabla^n = \left(-\frac{\sin\varphi}{\sin\theta}\frac{\partial}{\partial\varphi} + \cos\varphi\cos\theta\frac{\partial}{\partial\theta}, \frac{\cos\varphi}{\sin\theta}\frac{\partial}{\partial\varphi} + \sin\varphi\cos\theta\frac{\partial}{\partial\theta}, -\sin\theta\frac{\partial}{\partial\theta} \right). \tag{6}$$

Decomposition of the operators $\vec{r}$ and ∇ into the radial and angular parts simplifies expressions for the operators representing other observables. This is described in detail in Appendix A.

We separate the radial and angular variables also in the wave function

$$\langle\vec{r}|n,l,m\rangle = \langle r|n,l\rangle\langle\vec{n}|l,m\rangle = R_{n,l}(r/n)Y_{l,m}(\vec{n}). \tag{7}$$

It will be clear later why we write the argument of the radial function as r/n. By inserting this separation into Eq. (1) and using Eqs. (A8) and (A9) of Appendix A, we obtain the well-known equation for the radial functions

$$\left[\frac{p_r^2}{2} + \frac{l(l+1)}{2r^2} - \frac{1}{r}\right]R_{n,l}(r/n) = -\frac{1}{2n^2}R_{n,l}(r/n). \tag{8}$$

Here, p_r denotes the radial momentum

$$p_r = -i\left(\frac{\partial}{\partial r} + \frac{1}{r}\right). \tag{9}$$

At this point, the differential equation (8) is usually solved. However, there is another approach based on the commutativity of the Runge-Lenz vector with the Hamiltonian (2). The latter approach will prove to be more advantageous when dealing with many-electron atoms.

The Runge-Lenz vector is given by

$$\vec{X} = \frac{1}{2}(\vec{L}\times\vec{p} - \vec{p}\times\vec{L}) + \vec{n}, \tag{10}$$

Using the decompositions (3) and (5), it can be rewritten into the more suitable form

$$\vec{X} = \vec{n}\left(-1 - \frac{\partial}{\partial r} + \frac{L^2}{r}\right) + \nabla^n\frac{\partial}{\partial r}. \tag{11}$$

Commutativity of the components of Runge-Lenz vector with Hamiltonian (2) can be proved using Eqs. (A14) and (A15) of Appendix A and Eq. (11).

It is seen from Eq. (11) that the Runge-Lenz vector acts on spherical harmonics in the same way as the operator

$$\vec{V} = f(r)\vec{n} + g(r)\nabla^n. \tag{12}$$

Here, $f(r)$ and $g(r)$ are operators acting on radial functions. It follows from the representation theory of so(4) algebra that the third component of the operator (12) acts on the spherical harmonics as [see Eqs. (A28) and (A32) of Appendix A]

$$V_3|l,m\rangle = c_l\sqrt{(l+m)(l-m)}|l-1,m\rangle + c_{l+1}\sqrt{(l+1+m)(l+1-m)}|l+1,m\rangle. \tag{13}$$

The coefficients c_l are determined from Eq. (A34) of Appendix A

$$c_l^2(2l-1)(l+m) + c_{l+1}^2(l+1-m)(2l+3) = \langle l,m|(V^2 - i[V_1,V_2])|l,m\rangle. \tag{14}$$

Runge-Lenz vector commutes with Hamiltonian (2). Thus, Eqs. (13) and (14) can be in this case written as

$$X_3|n,l,m\rangle = c_l^n\sqrt{(l+m)(l-m)}|n,l-1,m\rangle + c_{l+1}^n\sqrt{(l+1+m)(l+1-m)}|n,l+1,m\rangle \tag{15}$$

and

$$\begin{aligned}(c_l^n)^2(2l-1)(l+m) + (c_{l+1}^n)^2(l+1-m)(2l+3) &= \langle n,l,m|(X^2 - i[X_1,X_2])|n,l,m\rangle \\ &= \langle n,l,m|1 + 2H(L^2+1) - 2HL_3|n,l,m\rangle \\ &= \frac{n^2 - l(l+1) - 1 + m}{n^2}.\end{aligned} \tag{16}$$

Comparing the terms proportional to the zeroth and first power of m on both sides of the last equation yields

$$c_l^n = \frac{1}{n}\sqrt{\frac{(n-l)(n+l)}{(2l+1)(2l-1)}}. \tag{17}$$

Expressions for X^2 and $[X_1,X_2]$ used in Eq. (16) can be obtained from Eqs. (1) and (11) and from Eqs. (A1), (A2), (A4)–(A6), (A9), (A10), and (A13)–(A15) of Appendix A.

Since operator $\vec{X}$ is Hermitian and its third component is real, coefficients c_l^n have to be real. It is seen from the last equation and Eq. (15) that this holds only if the maximum allowed value of l for fixed n is $l=n-1$ and n is an integer. This finishes the derivation of Bohr formula for the energy levels of the hydrogen atom. The derivation given here is more or less the same as that of Pauli [14]. Let us also note that six operators $\vec{L}$ and $\vec{X}$ are closed under commutation. This is usually referred to as so(4) algebra [13].

B. Wave functions of the hydrogen atom

We would like to point out that we can also derive the form of radial functions $R_{n,l}(r)$ without solving Eq. (8). We compare the action of operator X_3 on the states $|n,l,m\rangle$ as calculated from Eq. (11) and from Eq. (15). To get the action of operator X_3 given by Eq. (11) we need to know the action of operators n_3 and ∇_3^n on spherical harmonics. Operator $\vec{n}$ is special case of operator (12). The matrix elements of the operator n_3 are given by Eqs. (13) and (14). Since obviously $n^2=1$ and $[n_1,n_2]=0$ we have

$$n_3|l,m\rangle = b_{l,m}|l-1,m\rangle + b_{l+1,m}|l+1,m\rangle, \tag{18}$$

where

$$b_{l,m} = \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}}. \tag{19}$$

The action of the third component of operator ∇^n follows from Eq. (A16) of Appendix A and Eq. (18)

$$\nabla_3^n|l,m\rangle = (l+1)b_{l,m}|l-1,m\rangle - lb_{l+1,m}|l+1,m\rangle. \quad (20)$$

Using Eqs. (11), (18), and (20), we get that the third component of the Runge-Lenz vector acts on the states (7) as

$$X_3\langle\vec{r}|n,l,m\rangle = \left(l\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right)R_{n,l}(r/n)b_{l,m}Y_{l-1,m}(\vec{n}) - \left(-(l+1)\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right) \times R_{n,l}(r/n)b_{l+1,m}Y_{l+1,m}(\vec{n}). \quad (21)$$

Finally, we insert the separation (7) into Eq. (15). Since the spherical harmonics form an orthonormal basis set, the terms proportional to $Y_{l-1,m}(\vec{n})$ in Eqs. (15) and (21) have to be equal:

$$\left(l\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right)R_{n,l}(r/n) = \frac{\sqrt{n^2-l^2}}{n}R_{n,l-1}(r/n). \quad (22)$$

The terms proportional to $Y_{l+1,m}(\vec{n})$ in Eqs. (15) and (21) have to be equal as well, i.e.,

$$\left((l+1)\frac{d}{dr} + 1 - \frac{l(l+1)}{r}\right)R_{n,l}(r/n) = -\frac{\sqrt{n^2-(l+1)^2}}{n}R_{n,l+1}(r/n). \quad (23)$$

Considering the last equation for $l=n-1$, we get the first order differential equation for the radial function $R_{n,n-1}(r)$, whose solution reads

$$R_{n,n-1}(r/n) = K_n(r/n)^{n-1}e^{-r/n}. \quad (24)$$

Considering Eq. (22) for l descending from $n-1$ to 0, the remaining radial functions $R_{n,l}(r/n)$ are obtained by differentiation. Equations (22) and (23) were also derived in Ref. [18] from different considerations. In that paper it is described how these equations can be used for the calculation of the intensities of the hydrogen atom.

III. STURMIAN BASIS SET

In this section, the transition from the discrete part of the hydrogenic basis set to the Sturmian basis set is performed via energy-dependent scaling. The ladder operators for the radial functions are constructed. These operators yield the recurrence relations for the radial functions with the same orbital number l. These recurrence relations for the radial functions are combined with those derived in the previous Section to generate additional recurrence relations. Finally, the orthonormality relations of the Sturmian basis set are discussed.

A. Energy-dependent scaling

For variational calculation of the more complicated atoms the hydrogenic functions are not convenient. The reason is that the Hamiltonian given by Eq. (2) has both discrete and continuous spectra. Therefore, the discrete spectrum does not form a complete basis set. The incompleteness of the discrete hydrogenic functions is caused by the presence of factor $1/n$ in the argument of the exponential function, see Eq. (24). Therefore we make the energy-dependent scaling $r\to rn$. Equation (8) then takes the form

$$\left[\frac{p_r^2}{2} + \frac{l(l+1)}{2r^2} - \frac{n}{r}\right]R_{n,l}(r) = -\frac{1}{2}R_{n,l}(r). \quad (25)$$

In Eq. (8), we considered different energy levels labeled by n for fixed nuclear charge $Z=1$, while in Eq. (25), we consider different nuclear charges $Z=n$ for fixed energy level $E=-1/2$.

If we multiply Eq. (25) by r we can rewrite it into the form of the eigenvalue problem

$$T_3R_{n,l}(r) = nR_{n,l}(r), \quad (26)$$

where

$$T_3 = \frac{r}{2}\left(p_r^2 + \frac{l(l+1)}{r^2}\right) + \frac{r}{2}. \quad (27)$$

B. Ladder operators for radial functions

The great advantage of Eq. (26) is that the spectrum of operator T_3 is purely discrete. This is most easily seen by constructing step-up and step-down operators

$$T_\pm = \frac{r}{2}\left(p_r^2 + \frac{l(l+1)}{r^2}\right) - \frac{r}{2} \pm irp_r. \quad (28)$$

It follows from Eqs. (27) and (28) that

$$[T_3, T_\pm] = \pm T_\pm. \quad (29)$$

Acting with this operator equation on the radial functions $R_{n,l}(r)$, we get (see, e.g., Refs. [13,19,20])

$$T_\pm R_{n,l}(r) = \sqrt{(n\pm l\pm 1)(n\mp l)}R_{n\pm 1,l}(r). \quad (30)$$

Operators T_3 and $T_\pm$ are closed under commutation. This is related to the existence of the radial so(2,1) algebra, as detailed in Refs. [13,17,19]. With the help of operators T_3 and $T_\pm$ we can, for example, determine action of the radial coordinate and derivative with respect to radial coordinate on the radial functions, namely,

$$2rR_{n,l}(r) = (2T_3 - T_+ - T_-)R_{n,l}(r) = 2nR_{n,l}(r) - \sqrt{(n+l+1)(n-l)}R_{n+1,l}(r) - \sqrt{(n-l-1)(n+l)}R_{n-1,l}(r) \quad (31)$$

and

$$2r\left(\frac{d}{dr} + \frac{1}{r}\right)R_{n,l}(r) = (T_+ - T_-)R_{n,l}(r) = \sqrt{(n+l+1)(n-l)}R_{n+1,l}(r) - \sqrt{(n-l-1)(n+l)}R_{n-1,l}(r), \quad (32)$$

respectively. These equations follow from Eqs. (9), (26)–(28), and (30).

C. Recurrence relations

In the previous section we derived recurrence relations for the radial functions of hydrogen, Eqs. (22) and (23). By making energy-dependent scaling $r \to rn$ in these equations we convert them to the equations for the Sturmian radial functions

$$\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)-\frac{n}{l}r+l\right]R_{n,l}(r)=\frac{\sqrt{n^2-l^2}}{l}rR_{n,l-1}(r) \quad (33)$$

and

$$\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)+\frac{n}{l+1}r-(l+1)\right]R_{n,l}(r) = \frac{\sqrt{n^2-(l+1)^2}}{l+1}rR_{n,l+1}(r). \quad (34)$$

Thus, Eqs. (31) and (32) connect the radial functions with the same l and different n. The last two equations connect the radial functions with the same n and different l. We could have finished at this point. However, for the purposes of the following Section it is advantageous to combine Eqs. (31)–(34) to additional recurrence relations.

We apply Eqs. (31) and (32) to the left-hand side of the last two equations. After some manipulation we obtain

$$\begin{aligned}2rR_{n,l}(r) &= \sqrt{(n+l+1)(n+l+2)}R_{n+1,l+1}(r) \\ &\quad + \sqrt{(n-l-2)(n-l-1)}R_{n-1,l+1}(r) \\ &\quad - 2\sqrt{n^2-(l+1)^2}R_{n,l+1}(r)\end{aligned} \quad (35)$$

and

$$\begin{aligned}2rR_{n,l}(r) &= \sqrt{(n-l)(n+1-l)}R_{n+1,l-1}(r) \\ &\quad + \sqrt{(n+l)(n+l-1)}R_{n-1,l-1}(r) - 2\sqrt{n^2-l^2}R_{n,l-1}(r).\end{aligned} \quad (36)$$

Further, we rewrite Eqs. (33) and (34):

$$r\left(\frac{d}{dr}+\frac{l+1}{r}\right)R_{n,l}(r)=\frac{\sqrt{n^2-l^2}}{l}rR_{n,l-1}(r)+\frac{n}{l}rR_{n,l}(r) \quad (37)$$

and

$$r\left(\frac{d}{dr}-\frac{l}{r}\right)R_{n,l}(r)=\frac{\sqrt{n^2-(l+1)^2}}{l+1}rR_{n,l+1}(r)+\frac{n}{l+1}rR_{n,l}(r) \quad (38)$$

and arrange the right-hand sides of the last two equations as follows. In Eq. (37) we use Eq. (31) on the first term and Eq. (36) on the second term. In Eq. (38) we use Eq. (31) on the first term and Eq. (35) on the second term. After some manipulation we get

$$\begin{aligned}2r\left(\frac{d}{dr}-\frac{l}{r}\right)R_{n,l}(r) &= -\sqrt{(n+l+1)(n+l+2)}R_{n+1,l+1}(r) \\ &\quad + \sqrt{(n-l-2)(n-l-1)}R_{n-1,l+1}(r)\end{aligned} \quad (39)$$

and

$$\begin{aligned}2r\left(\frac{d}{dr}+\frac{l+1}{r}\right)R_{n,l}(r) &= -\sqrt{(n-l)(n+1-l)}R_{n+1,l-1}(r) \\ &\quad + \sqrt{(n+l)(n+l-1)}R_{n-1,l-1}(r).\end{aligned} \quad (40)$$

Equations (31), (32), (35), (36), (39), and (40) will be used for the calculation of one- and two-electron integrals in the next section.

D. Orthonormality relations

Since functions $R_{n,l}(r)$ are eigenfunctions of Hermitian operator T_3, they form an orthonormal basis set. However, in contrast to the Hamilton operator (2) that is Hermitian with respect to the inner product

$$\langle n_1,l|H|n_2,l\rangle=\int_0^\infty r^2R_{n_1,l}(r)HR_{n_2,l}(r)dr, \quad (41)$$

operator T_3 is Hermitian with respect to the inner product

$$(n_1,l|T_3|n_2,l)=\int_0^\infty rR_{n_1,l}(r)T_3R_{n_2,l}(r)dr. \quad (42)$$

Consequently, while the wave functions of hydrogen are orthonormal with respect to the inner product

$$\langle n_1,l|n_2,l\rangle=\int_0^\infty r^2R_{n_1,l}(r)R_{n_2,l}(r)dr=\delta_{n_1,n_2}, \quad (43)$$

the eigenfunctions $R_{n,l}(r)$ of operator T_3 are orthonormal with respect to the inner product

$$(n_1,l|n_2,l)=\int_0^\infty rR_{n_1,l}(r)R_{n_2,l}(r)dr=\delta_{n_1,n_2}. \quad (44)$$

IV. MATRIX ELEMENTS OF THE COULOMB INTERACTION

In this section, we apply results of the previous section to the calculation of two-electron integrals. First, as usually, we separate the radial and angular degrees of freedom by means of the multipole expansion. Further, we write the product of two radial functions as a linear combination of radial functions. We thus reduce the integrals over four radial functions to the integrals over two radial functions. For these reduced integrals, we derive recurrence relations combining integration by parts with algebraic methods. Using result of this section calculation of two-electron integrals is reduced to the calculation of one-electron integrals. Evaluation of one-electron integrals is described in Appendix B.

A. Screened radial functions

In many-electrons atoms the electrons occupying different orbitals "see" different effective nuclear charges. For example, the dominant configuration of P states of two electron atoms is the one in which the first electron occupies the *s* orbital and the second electron occupies the *p* orbital. Now, the electron occupying the *s* orbital is close to the nucleus and its effective nuclear charge is close to the nuclear charge Z. However, the electron occupying the *p* orbital is further away from the nucleus and "sees" the charge Z of nucleus "screened" by the charge of the electron in *s* orbital -1. Its effective nuclear charge is therefore close to $Z-1$. Thus, to get fast convergence of the variational method, we have to consider different screening constants for different electrons.

For this purpose, instead of the "ordinary" radial functions $R_{n,l}(r)$, we consider the "screened" radial functions $R_{n,l}(\xi r)$. The "screened" functions are obtained from "ordinary" functions by the energy-independent scaling $r \to \xi r$ and multiplication by ξ. This multiplication is to ensure the proper normalization (44). For example, the nodeless "screened" functions $R_{l+1,l}(\xi r)$ read

$$R_{l+1,l}(\xi r) = \frac{2\xi}{\sqrt{(2l+1)!}}(2\xi r)^l e^{-\xi r}. \qquad (45)$$

This equation is obtained from Eq. (24) for $r \to rn\xi$ and from Eq. (44).

B. Separation of radial and angular degrees of freedom

Calculating the matrix elements of the Coulomb interaction between two spin orbitals leads to the calculation of the integrals

$$\int d^3r_1 \int d^3r_2 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) Y_{l_{1k},m_{1k}}(\vec{n}_1) R_{n_{2k},l_{2k}}(r_2\xi_{2k}) \times Y_{l_{2k},m_{2k}}(\vec{n}_2) r_{12}^{-1} R_{n_{1j},l_{1j}}(r_1\xi_{1j}) Y_{l_{1j},m_{1j}}(\vec{n}_1) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) \times Y_{l_{2j},m_{2j}}(\vec{n}_2). \qquad (46)$$

To separate the angular and radial degrees of freedom, we expand r_{12}^{-1} in the multipole expansion

$$r_{12}^{-1} = \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\vec{n}_1 \cdot \vec{n}_2), \qquad (47)$$

where $r_< = r_1$, $r_> = r_2$ if $r_1 < r_2$ and $r_< = r_2$, $r_> = r_1$ if $r_1 > r_2$. Here, $P_l(x)$ denotes the Legendre polynomials.

The angular part of the integration is achieved by the methods developed by Racah, see, e.g., Refs. [9–11]. The radial part of the integration involves calculation of integrals

$$\int_0^\infty dr_1 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j}) r_1^{l+2} \times \int_{r_1}^\infty dr_2 R_{n_{2k},l_{2k}}(r_2\xi_{2k}) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) r_2^{-l+1} + \int_0^\infty dr_1 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j}) r_1^{-l+1} \times \int_0^{r_1} dr_2 R_{n_{2k},l_{2k}}(r_2\xi_{2k}) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) r_2^{l+2}. \qquad (48)$$

C. Linearization of the product of two functions

It has been pointed out in Ref. [17], that the products of the radial functions of the same variable [such as $R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j})$] appear in the integrals (48). The integration of the product of three spherical harmonics is greatly simplified by virtue of the fact that the product of two spherical harmonics can be written as a linear combination of spherical harmonics. This is known as a special case of the Wigner-Eckart theorem. Being inspired by that theorem, we write

$$r^p R_{n_1,l_1}(\xi_1 r) R_{n_2,l_2}(\xi_2 r) = \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p R_{n,l'}(\xi r), \qquad (49)$$

where $l' = l_1 + l_2$ and $\xi = \xi_1 + \xi_2$. The number of the nodes of function $R_{n,l'}(\xi r)$ is $n - l' - 1$. The product of the function with $n_1 - l_1 - 1$ nodes and the function with $n_2 - l_2 - 1$ nodes is the function with $n_1 + n_2 - 1 - l' - 1$ nodes. Thus, this function is composed only of the functions $R_{n,l'}(\xi r)$ for which the number of nodes $n - l' - 1$ does not exceed $n_1 + n_2 - 1 - l' - 1$. Thus, the upper bound in the summation in Eq. (49) is $n = n_1 + n_2 - 1$ for $p=0$. For a nonzero p the upper bound is deduced from Eq. (31).

Let us determine coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p$. Multiplying Eq. (49) by $rR_{n',l'}(\xi r)$, integrating over r and using the orthonormality of radial functions, (44), we obtain

$$(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n')_p = \int_0^\infty r^{p+1} R_{n',l'}(\xi r) R_{n_1,l_1}(\xi_1 r) R_{n_2,l_2}(\xi_2 r) dr. \qquad (50)$$

Further, we multiply Eq. (49) by $2r$. On the left-hand side of Eq. (49) we let $2r$ act on the function $R_{n_1,l_1}(\xi_1 r)$ according to Eq. (31) where we substitute $r \to \xi_1 r$. On the right-hand side of Eq. (49) operator $2r$ acts on function $R_{n,l'}(\xi r)$. Thus we arrive at equation

$$r^p R_{n_2,l_2}(\xi_2 r)\frac{1}{\xi_1}[2n_1 R_{n_1,l_1}(\xi_1 r) - \sqrt{(n_1+l_1+1)(n_1-l_1)} R_{n_1+1,l_1}(\xi_1 r) - \sqrt{(n_1-l_1-1)(n_1+l_1)} R_{n_1-1,l_1}(\xi_1 r)]$$

$$
\begin{aligned}
&= \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \frac{1}{\xi} \\
&\quad \times[2nR_{n,l'}(\xi r) - \sqrt{(n+l'+1)(n-l')}R_{n+1,l'}(\xi r) \\
&\quad - \sqrt{(n-l'-1)(n+l')}R_{n-1,l'}(\xi r)]. \qquad (51)
\end{aligned}
$$

We multiply the last equation by $rR_{n',l'}(\xi r)$, integrate over r and use the orthonormality relations (44) and Eq. (50):

$$
\begin{aligned}
&2n_1(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n') \\
&\quad - \sqrt{(n_1+l_1+1)(n_1-l_1)}(n_1+1,l_1,\xi_1,n_2,l_2,\xi_2|n') \\
&\quad - \sqrt{(n_1-l_1-1)(n_1+l_1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n') \\
&\quad = \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \frac{\xi_1}{\xi} \\
&\quad \times[2n\delta_{n',n} - \sqrt{(n+l'+1)(n-l')}\delta_{n',n+1} \\
&\quad - \sqrt{(n-l'-1)(n+l')}\delta_{n',n-1}]. \qquad (52)
\end{aligned}
$$

After deleting the zero terms on the right-hand side, we obtain the following recurrence relation for the coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)$

$$
\begin{aligned}
&(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p\sqrt{(n_1-l_1-1)(n_1+l_1)} \\
&\quad = 2\left(n_1-1-\frac{\xi_1 n}{\xi}\right)(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \\
&\qquad - \sqrt{(n_1+l_1-1)(n_1-l_1-2)}(n_1-2,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \\
&\qquad + \frac{\xi_1}{\xi}\sqrt{(n+l')(n-l'-1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n-1)_p \\
&\qquad + \frac{\xi_1}{\xi}\sqrt{(n-l')(n+l'+1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n+1)_p. \qquad (53)
\end{aligned}
$$

The last equation expresses coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p$ through coefficients $(n_1',l_1,\xi_1,n_2,l_2,\xi_2|n')_p$ with n_1' smaller than n_1, but with n' sometimes smaller and sometimes larger than n. But since there are lower and upper bounds on the possible values of n, see Eq. (49), Eq. (53) can be used to lower the quantum number n_1 to l_1+1. To lower the quantum number n_2 to l_2+1 we apply Eq. (53) again exchanging this time n_1 and n_2, l_1 and l_2, and ξ_1 and ξ_2 and taking into account that $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p=(n_2,l_2,\xi_2,n_1,l_1,\xi_1|n)_p$.

The value of coefficients $(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_p$ is obtained by inserting Eq. (45) into Eq. (49). We thus obtain

$$
\begin{aligned}
&(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+1)_0 \\
&\quad = \frac{2\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+1}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}} \qquad (54)
\end{aligned}
$$

and

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_0 = 0, n > l_1+l_2+1. \qquad (55)$$

The case of a nonzero p is obtained from Eqs. (49) and (31). For example,

$$
\begin{aligned}
&(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+1)_1 \\
&\quad = 2(l_1+l_2+1)\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}, \qquad (56)
\end{aligned}
$$

$$
\begin{aligned}
&(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+2)_1 \\
&\quad = -\sqrt{2(l_1+l_2+1)}\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}, \qquad (57)
\end{aligned}
$$

and

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_1 = 0, \quad n > l_1+l_2+2. \qquad (58)$$

Remarkably, the described method of calculating coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p$ is numerically stable.

Using Eq. (49) for $p=1$, the integrals (48) can be written as linear combination of the integrals [17]

$$P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2) + P_{N_2,N_1}^{L_2,L_1,l}(\xi_2,\xi_1). \qquad (59)$$

Here,

$$P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2) = \int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1)r_1^{l+1}\int_{r_1}^\infty \tilde{R}_{N_2,L_2}(\xi_2 r_2)r_2^{-l}\,dr_2\,dr_1 \qquad (60)$$

and

$$
\begin{aligned}
P_{N_2,N_1}^{L_2,L_1,l}(\xi_2,\xi_1) &= \int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1)r_1^{-l} \\
&\quad \times\int_0^{r_1} \tilde{R}_{N_2,L_2}(\xi_2 r_2)r_2^{l+1}\,dr_2\,dr_1, \qquad (61)
\end{aligned}
$$

where we introduced the unnormalized radial functions $\tilde{R}_{n,l}(r)$ related to the normalized functions $R_{n,l}(r)$ via relation

$$\tilde{R}_{n,l}(r) = \sqrt{\frac{(n+l)!}{(n-l-1)!}}R_{n,l}(r). \qquad (62)$$

By using unnormalized functions the irrational factors are conveniently eliminated.

The great advantage of our procedure is that the integrals (60) can be evaluated much more easily than the original integrals (48). In the next subsection, we derive recurrence relations for these integrals.

D. Recurrence relations for the integrals

1. Recurrence relations connecting integrals with different values of N_2 and L_2

The recurrence relations connecting integrals (60) with different values of N_2 and L_2 are derived from "analytic" equation [17]

$$\int_{r_1}^{\infty} r_2\left(\frac{d}{dr_2}+\frac{1}{r_2}\right)[r_2^{-l}\tilde{R}_{N_2,L_2}(\xi_2 r_2)]dr_2=-r_1^{-l+1}\tilde{R}_{N_2,L_2}(\xi_2 r_1) \tag{63}$$

obtained by integration by parts and from the "algebraic" equations

$$2r\left(\frac{d}{dr}+\frac{1}{r}\right)\tilde{R}_{n,l}(\xi r)=(n-l)\tilde{R}_{n+1,l}(\xi r)-(n+l)\tilde{R}_{n-1,l}(\xi r), \tag{64}$$

$$2r\left(\frac{d}{dr}-\frac{l}{r}\right)\tilde{R}_{n,l}(r)=-\tilde{R}_{n+1,l+1}(r)+\tilde{R}_{n-1,l+1}(r), \tag{65}$$

and

$$2r\left(\frac{d}{dr}+\frac{l+1}{r}\right)\tilde{R}_{n,l}(r)=-(n-l)(n+1-l)\tilde{R}_{n+1,l-1}(r)+(n+l)\times(n+l-1)\tilde{R}_{n-1,l-1}(r). \tag{66}$$

Equations (64)–(66) are obtained by substituting Eq. (62) into Eqs. (32), (39), and (40).

Inserting Eqs. (64)–(66) into Eq. (63), multiplying Eq. (63) by $2\tilde{R}_{N_1,L_1}(r_1\xi_1)r_1^{l+1}$ and integrating over r_1 from zero to infinity we obtain successively

$$\begin{aligned}-(N_2+L_2)&P^{L_1,L_2,l}_{N_1,N_2-1}(\xi_1,\xi_2)\\&+(N_2-L_2)P^{L_1,L_2,l}_{N_1,N_2+1}(\xi_1,\xi_2)-2lP^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{67}$$

$$\begin{aligned}P^{L_1,L_2+1,l}_{N_1,N_2-1}&(\xi_1,\xi_2)\\&-P^{L_1,L_2+1,l}_{N_1,N_2+1}(\xi_1,\xi_2)+2(L_2+1-l)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{68}$$

and finally

$$\begin{aligned}(N_2+L_2)&(N_2+L_2-1)P^{L_1,L_2-1,l}_{N_1,N_2-1}(\xi_1,\xi_2)\\&-(N_2-L_2)(N_2-L_2+1)P^{L_1,L_2-1,l}_{N_1,N_2+1}(\xi_1,\xi_2)-2(L_2\\&+l)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned} \tag{69}$$

The one-electron integrals on the right-hand side of these equations are given as

$$(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2)=\int_0^{\infty}2r^2\tilde{R}_{N_1,L_1}(\xi_1 r)\tilde{R}_{N_2,L_2}(\xi_2 r)dr. \tag{70}$$

2. Recurrence relations connecting integrals with different values of N_1 and L_1

To derive recurrence relations connecting the integrals (60) with different values of N_1 and L_1, we need a modification of "analytic" equation (63), namely [17]

$$\begin{aligned}\int_0^{\infty}dr_1\, r_1\left(\frac{d}{dr_1}+\frac{1}{r_1}\right)[r_1^{l+1}\tilde{R}_{N_1,L_1}(\xi_1 r_1)]\int_{r_1}^{\infty}dr_2\,\tilde{R}_{N_2,L_2}(\xi_2 r_2)r_2^{-l}\\=\int_0^{\infty}dr_1 r_1^2\tilde{R}_{N_1,L_1}(\xi_1 r_1)\tilde{R}_{N_2,L_2}(\xi_2 r_1)\end{aligned} \tag{71}$$

obtained by integration by parts. By inserting the "algebraic" equations (64)–(66) into Eq. (71) we obtain

$$\begin{aligned}-(N_1+L_1)&P^{L_1,L_2,l}_{N_1-1,N_2}(\xi_1,\xi_2)\\&+(N_1-L_1)P^{L_1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2)+2(l+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{72}$$

$$\begin{aligned}P^{L_1+1,L_2,l}_{N_1-1,N_2}&(\xi_1,\xi_2)\\&-P^{L_1+1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2)+2(L_1+l+2)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{73}$$

and, finally,

$$\begin{aligned}(N_1+L_1)&(N_1+L_1-1)P^{L_1-1,L_2,l}_{N_1-1,N_2}(\xi_1,\xi_2)\\&-(N_1-L_1)(N_1-L_1+1)P^{L_1-1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2)\\&+2(l+1-L_1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned} \tag{74}$$

3. Discussion

By means of recurrence relations for the radial functions, we have derived recurrence relations for the integrals. We note that Eq. (67) and (72) were derived already in Ref. [17]. As is clear from the above derivation, these equations result from Eq. (64). The latter can be traced back to commutation relations (29). Equation (64) connects the radial functions with different principle numbers n but the same orbital number l. Consequently, Eqs. (67) and (72) connect the values of integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ with different principal numbers N_1 and N_2, but with the same orbital numbers L_1 and L_2. On the other hand, Eqs. (68), (69), (73), and (74) are derived for the first time here. They result from Eqs. (65) and (66). The latter can be traced back to the commutation relations between operators pertaining to so(4) algebra. Equations (65) and (66) connect the radial functions with different principle numbers n and with different orbital number l. Consequently, Eqs. (68), (69), (73), and (74) connect the values of integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ with different principal numbers N_1 and N_2 and with different orbital numbers L_1 and L_2.

In Ref. [17] we found by experimentation with MAPLE that Eqs. (67) and (72) acquire very simple solution in the cases when the right-hand side vanishes. This appears either for $\xi_1=\xi_2$, $L_1=L_2$ and $|N_1-N_2|>1$, see Eqs. (44) and (31), or for $\xi_1=\xi_2$, $L_1<L_2$ and $N_1>N_2+1$, see discussion after Eq. (B12) below. Further, we found that integrals $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)$ vanish for $N_1>N_2$. At that time we did not know Eqs. (68), (69), (73), and (74). The information found by experimentation is contained in these equations.

Now, we have to use Eqs. (67)–(74) for the actual calculation of integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ in such a way that the simplification mentioned above comes out in a numerical stable way. For example, as mentioned above, integrals $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)$ equal zero for $N_1>N_2$. This zero cannot result from a subtraction of two large numbers.

With this in mind we combine Eqs. (67) and (68) into a single equation

$$\begin{aligned}&-2lP^{L_1,L_2+1,l}_{N_1,N_2}(\xi_1,\xi_2)-2(L_2+1)P^{L_1,L_2+1,l}_{N_1,N_2+1}(\xi_1,\xi_2)\\&\quad+2(L_2+1-l)(N_2+L_2+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2+1,\xi_2)\\&\qquad-(N_2+L_2+1)(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned}\tag{75}$$

The right-hand side of this equation can be brought into the form

$$-\frac{2(L_2+1)}{\xi_2}[(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)-(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)],$$

where

$$(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=\int_0^\infty r\tilde{R}_{N_1,L_1}(\xi_1 r)\tilde{R}_{N_2,L_2}(\xi_2 r)dr.\tag{76}$$

Here, we used equations

$$2\xi_2 r\tilde{R}_{N_2,L_2}(\xi_2 r)=\tilde{R}_{N_2+1,L_2+1}(\xi_2 r)+\tilde{R}_{N_2-1,L_2+1}(\xi_2 r)-2\tilde{R}_{N_2,L_2+1}(\xi_2 r)\tag{77}$$

and

$$\begin{aligned}&2\xi_2 r\tilde{R}_{N_2,L_2+1}(\xi_2 r)\\&\quad=2N_2\tilde{R}_{N_2,L_2+1}(\xi_2 r)\\&\qquad-(N_2-L_2-1)\tilde{R}_{N_2+1,L_2+1}(\xi_2 r)\\&\qquad-(N_2+L_2+1)\tilde{R}_{N_2-1,L_2+1}(\xi_2 r).\end{aligned}\tag{78}$$

These equations were obtained by substituting Eq. (62) into Eqs. (31) and (35), respectively.

Further, we combine Eqs. (67) and (69) into a single equation

$$\begin{aligned}&2L_2(N_2+L_2-1)P^{L_1,L_2-1,l}_{N_1,N_2-1}(\xi_1,\xi_2)\\&\quad-2l(N_2-L_2)P^{L_1,L_2-1,l}_{N_1,N_2}(\xi_1,\xi_2)-2(L_2+l)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2-1,\xi_2)(N_2-L_2)\\&\qquad-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned}\tag{79}$$

The right-hand side of this equation can be simplified into the form

$$\begin{aligned}&-\frac{2L_2}{\xi_2}[(N_2+L_2-1)(N_1,L_1,\xi_1|N_2-1,L_2-1,\xi_2)\\&\quad-(N_2-L_2)(N_1,L_1,\xi_1|N_2,L_2-1,\xi_2)].\end{aligned}$$

Here we used Eq. (78) and equation

$$\begin{aligned}2\xi_2 r\tilde{R}_{N_2,L_2}(\xi_2 r)&=(N_2-L_2+1)(N_2-L_2)\tilde{R}_{N_2+1,L_2-1}(\xi_2 r)\\&\quad+(N_2+L_2)(N_2+L_2-1)\tilde{R}_{N_2-1,L_2-1}(\xi_2 r)\\&\quad-2(N_2+L_2)(N_2-L_2)\tilde{R}_{N_2,L_2-1}(\xi_2 r).\end{aligned}\tag{80}$$

This equation is obtained by inserting Eq. (62) into Eq. (36).

Similarly, we put together Eqs. (72) and (73)

$$\begin{aligned}&-2(L_1+1)P^{L_1+1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2)+2(l+1)P^{L_1+1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad+2(L_1+l+2)(N_1+L_1+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=\frac{2(L_1+1)}{\xi_1}[(N_1+1,L_1+1,\xi_1|N_2,L_2,\xi_2)\\&\qquad-(N_1,L_1+1,\xi_1|N_2,L_2,\xi_2)],\end{aligned}\tag{81}$$

and Eqs. (72) and (74)

$$\begin{aligned}&2L_1(N_1+L_1-1)P^{L_1-1,L_2,l}_{N_1-1,N_2}(\xi_1,\xi_2)+2(N_1-L_1)(l+1)\\&\quad\times P^{L_1-1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)+2(l+1-L_1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=\frac{2L_1}{\xi_1}[(N_1+L_1-1)(N_1-1,L_1-1,\xi_1|N_2,L_2,\xi_2)\\&\qquad-(N_1-L_1)(N_1,L_1-1,\xi_1|N_2,L_2,\xi_2)].\end{aligned}\tag{82}$$

We note that considering the last equation for $\xi_2=\xi_1$ and $L_1=l+1$ together with orthonormality relations (44) yields $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)=0$ in a numerically stable way, as desired.

E. Actual calculations of the integrals

The above equations can be used for actual calculations of the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ as follows. We set $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)=0$ whenever $N_1<L_1+1$ or $N_2<L_2+1$. Further, we assume that we know how to calculate the one-electron integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$. Calculation of these integrals is left to Appendix B.

1. Case $L_1\neq L_2$

We can use Eq. (81) repeatedly to lower the value of L_1 to l and to consider Eq. (82) for $L_1=l+1$ to calculate the integrals $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$. Similarly, we can use Eq. (75) repeatedly to lower the value of L_2 to l and to consider Eq. (75) for $L_2=l-1$ to calculate the integrals $P^{L_1,l,l}_{N_1,N_2}(\xi_1,\xi_2)$. However, this way of calculation of the integrals changes the difference L_1-L_2. This is not advantageous because of the following reason. As mentioned above, the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ have particularly simple form for $\xi_1=\xi_2$ and $L_1=L_2$. Proceeding in this way we would calculate simple integrals $P^{L_1,L_1,l}_{N_1,N_2}(\xi_1,\xi_1)$ through the more complicated integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)$ with $L_1\neq L_2$.

The better way is to reduce the integrals with $L_1 \neq L_2$ only to the case $L_1 = L_2$. In the case L_1 greater than L_2 we use Eq. (81) repeatedly to lower the value of L_1 to L_2. In the opposite case L_2 greater than L_1 we use Eq. (75) to lower the value of L_2 to L_1.

2. Case $L_1 = L_2 > l$

Further, we show that the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ for the case $L_1 = L_2 > l$ can be reduced to the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ with $L_1 = L_2 = l$. We set $L_1 = L$ and $L_2 + 1 = L$ in Eqs. (75) and (82). We eliminate the integrals $P^{L,L-1,l}_{N_1,N_2}(\xi_1,\xi_2)$ from these equations and obtain

$$\begin{aligned}
&LP^{L,L,l}_{N_1,N_2+1}(\xi_1,\xi_2) + lP^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2) \\
&\quad - \frac{L}{\xi_2}[(N_1,L,\xi_1|N_2+1,L,\xi_2) - (N_1,L,\xi_1|N_2,L,\xi_2)] \\
&\quad = \frac{(L-l)(N_2+L)}{l+1-L}\Bigg\{ -L(N_1+L-1)P^{L-1,L-1,l}_{N_1-1,N_2}(\xi_1,\xi_2) \\
&\qquad - (N_1-L)(l+1)P^{L-1,L-1,l}_{N_1,N_2}(\xi_1,\xi_2) \\
&\qquad + \frac{L}{\xi_1}[(N_1+L-1)(N_1-1,L-1,\xi_1|N_2,L-1,\xi_2) \\
&\qquad - (N_1-L)(N_1,L-1,\xi_1|N_2,L-1,\xi_2)]\Bigg\}. \qquad (83)
\end{aligned}$$

This equation cannot be used in the case $L = l+1$, since the denominator on the right-hand side vanishes.

Further, we set $L_1 + 1 = L$ and $L_2 = L$ in Eqs. (79) and (81). We eliminate integrals $P^{L-1,L,l}_{N_1,N_2}(\xi_1,\xi_2)$ from these equations and obtain

$$\begin{aligned}
&LP^{L,L,l}_{N_1+1,N_2}(\xi_1,\xi_2) - (l+1)P^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2) \\
&\quad + \frac{L}{\xi_1}[(N_1+1,L,\xi_1|N_2,L,\xi_2) - (N_1,L,\xi_1|N_2,L,\xi_2)] \\
&\quad = \frac{(L+l+1)(N_1+L)}{l+L}\Bigg\{ -L(N_2+L-1)P^{L-1,L-1,l}_{N_1,N_2-1}(\xi_1,\xi_2) \\
&\qquad + l(N_2-L)P^{L-1,L-1,l}_{N_1,N_2}(\xi_1,\xi_2) \\
&\qquad + \frac{L}{\xi_2}[(N_2+L-1)(N_1,L-1,\xi_1|N_2,L-1,\xi_2) \\
&\qquad - (N_2-L)(N_1,L-1,\xi_1|N_2,L-1,\xi_2)]\Bigg\}. \qquad (84)
\end{aligned}$$

This equation can be used in all cases.

Using Eqs. (83) and (84) we calculate integrals $P^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2)$ through integrals $P^{L-k,L-k,l}_{N_1,N_2}(\xi_1,\xi_2)$. In actual calculation we use Eq. (83) in cases $N_2 < N_1$ and $L \neq l+1$. Otherwise we use Eq. (84). These equations are used repeatedly until $L-k=l$.

The advantage of Eqs. (83) and (84) is that they calculate integrals $P^{L_1,L_2}_{N_1,N_2}(\xi_1,\xi_2)$ where $L_1 = L_2$ through the integrals with different quantum numbers N_1, N_2, L_1, and L_2, but again with $L_1 = L_2$. The advantage of this approach becomes apparent when considering the case $\xi_1 = \xi_2$. By virtue of the orthonormality relations, (44), the one-electron integrals in Eqs. (83) and (84) nearly always vanish.

3. Case $L_1 = L_2 = l$

Setting $L_2 = l-1$ and $L_1 = l$ in Eq. (75) and setting $L_1 = l+1$ and $L_2 = l$ in Eq. (82) we obtain two equations for the integrals $P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2)$

$$\begin{aligned}
&P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2) + P^{l,l,l}_{N_1,N_2+1}(\xi_1,\xi_2) \\
&\quad = \frac{1}{\xi_2}[(N_1,l,\xi_1|N_2+1,l,\xi_2) - (N_1,l,\xi_1|N_2,l,\xi_2)] \qquad (85)
\end{aligned}$$

and

$$\begin{aligned}
&(N_1+l)P^{l,l,l}_{N_1-1,N_2}(\xi_1,\xi_2) + (N_1-l-1)P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2) \\
&\quad = \frac{1}{\xi_1}[(N_1+l)(N_1-1,l,\xi_1|N_2,l,\xi_2) \\
&\qquad - (N_1-l-1)(N_1-1,l,\xi_1|N_2,l,\xi_2)]. \qquad (86)
\end{aligned}$$

In the case when $N_1 < N_2$ and $N_1 > l+1$, we use the latter equation, otherwise we use the former one.

V. APPLICATION TO HELIUM

The method for calculation of the one- and two-electron matrix elements described in this paper is general and can be applied to all atoms, or more generally to all one-center integrals. To show that the method really works and can be used to obtain further insights into the atomic structure we apply it to the CI calculation of helium.

A. Algebraic formulation

The Schrödinger equation for the two-electron atoms in atomic units takes the form

$$\left[-\frac{\nabla^2_{(1)}}{2} - \frac{\nabla^2_{(2)}}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\psi = E\psi, \qquad (87)$$

where Z is the charge of the nucleus. In the case of helium we set $Z=2$. By scaling the coordinates of the electrons $\vec{x}^{(i)} \to Z^{-1}\vec{x}^{(i)}$, $i=1,2$, we get an equivalent equation

$$\left[-\frac{\nabla^2_{(1)}}{2} - \frac{\nabla^2_{(2)}}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z}\frac{1}{r_{12}}\right]\psi = \frac{E}{Z^2}\psi. \qquad (88)$$

Since Hamiltonian in Eq. (88) commutes with the components of the total angular momentum and spin of the electrons, it is advantageous to expand the exact wave function into the symmetry adapted basis functions

$$\begin{aligned}
\langle \vec{r}_1,\vec{r}_2|k\rangle &= R_{n_{1k},l_{1k}}(r_1\xi_{1k})R_{n_{2k},l_{2k}}(r_2\xi_{2k})\langle \vec{n}_1,\vec{n}_2|(l_{1k},l_{2k}),L,0\rangle \\
&\quad + (-1)^{L+S-l_{1k}-l_{2k}}R_{n_{1k},l_{1k}}(r_2\xi_{1k})R_{n_{2k},l_{2k}}(r_1\xi_{2k}) \\
&\quad \times \langle \vec{n}_2,\vec{n}_1|(l_{1k},l_{2k}),L,0\rangle, \qquad (89)
\end{aligned}$$

where $R_{n,l}(\xi r)$ are the Sturmian radial function used throughout the paper, $S=0$ refers to the singlets and $S=1$ to the triplets, and finally $|(l_1,l_2),L,0>$ are the eigenstates of the square of the total angular momentum

$$\langle\vec{n}_1,\vec{n}_2|(l_1,l_2),L,0\rangle = \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} (l_1,m,l_2,-m|L,0)Y_{l_1,m}(\vec{n}_1)Y_{l_2,-m}(\vec{n}_2).$$

Here, $(|)$ denotes the Clebsch-Gordan coefficients.

The calculation of the matrix elements of the operators in Eq. (88) between two functions of the form (89) is reduced either to the calculation of the two-electron integrals (46) or to the calculation of the one-electron integrals. One encounters two kinds of the one-electron integrals. The first one are the overlap integrals that are reduced to the integrals (70)

$$\int d^3r\, R_{n_1,l_1}(\xi_1 r)Y_{l_1,m_1}(\vec{n})R_{n_2,l_2}(\xi_2 r)Y_{l_2,m_2}(\vec{n}) = \sqrt{\frac{(n_1-l_1-1)!}{(n_1+l_1)!}\frac{(n_2-l_1-1)!}{(n_2+l_1)!}}(n_1,l_1,\xi_1|r|n_2,l_1,\xi_2). \tag{90}$$

The second one are the integrals involving the Laplace operator. These are calculated as follows:

$$\int d^3r\, R_{n_1,l_1}(\xi_1 r)Y_{l_1,m_1}(\vec{n})\left(-\frac{\nabla^2}{2}\right)R_{n_2,l_2}(\xi_2 r)Y_{l_2,m_2}(\vec{n}) = \xi_2\int_0^\infty rR_{n_1,l_1}(\xi_1/\xi_2 r)\frac{r}{2}\left(p_r^2+\frac{l_1(l_1+1)}{r^2}\right)R_{n_2,l_1}(r)dr = \sqrt{\frac{(n_1-l_1-1)!}{(n_1+l_1)!}\frac{(n_2-l_1-1)!}{(n_2+l_1)!}}\xi_2(n_1,l_1,\xi_1/\xi_2|T_3/2 + (T_+ + T_-)/4|n_2,l_1,1). \tag{91}$$

Here, we used an expression for the Laplacian operator in spherical coordinates (A8), equation for spherical harmonics (A9), orthonormality of spherical harmonics, and Eqs. (27) and (28). The resulting matrix elements are by means of Eqs. (26) and (30) reduced to the calculation of the overlap integrals (76).

B. Configuration interaction

In this paper we concentrate on calculation of S and P states, i.e., on the states with $L=0$ and $L=1$ in Eq. (89). It follows from properties of Clebsch-Gordan coefficients that for $L=0$ it must be $l_{1k}=l_{2k}=l_k$ and for $L=1$ it must be $l_{1k}=l_{2k}-1=l_k$. Thus, after taking into account all symmetries, we have an infinite number of configurations labeled by set of integers $\{n_{1k},n_{2k},l_k\}$, with k ranged from 1 to infinity. When performing CI calculation we have to truncate this basis set in some manner. Also, we are free to optimize the screening constants ξ_{1k} and ξ_{2k} for different l_k to achieve the rapid convergence of CI method.

In this paper we are mainly interested in the numerical stability of the integrals. The main source of the instabilities are the integrals among highly excited configurations. To know the integrals that have to be evaluated accurately, we need to know the highly excited configurations that contribute significantly. Also, we need to know the values of the screening constants that are close to the optimal ones.

Let us consider the second-order of the perturbation theory

$$E^{(2)} = \sum_{k=1}^{\infty}\frac{W_{k0}^2}{E_0^{(0)}-E_k^{(0)}}. \tag{92}$$

It is seen that if the matrix elements W_{k0} do not vary appreciably with the increasing k, the contributions of the configurations decrease with the increasing unperturbed energies $E_k^{(0} = -(n_{1k}^{-2}+n_{2k}^{-2})/2$. Now it is clear that, for example, $\{1s,(n+1)s\}$ configurations are more significant than $\{2s,(n+2)s\}$ and $\{2p,(n+2)p\}$ configurations. The latter are more significant than $\{3s,(n+3)s\}$, $\{3p,(n+3)p\}$, and $\{3d,(n+3)d\}$ configurations and so on. Generally, for the S states we consider $\{Nl,(N+n)l\}$ configurations with l going from 0 to $N-1$ and with n going from 0 (for the singlets) or from 1 (for the triplets) to some b. For the P states we consider two kinds of configurations: either $\{Nl,(N+n)(l+1)\}$ with l going from 0 to $N-1$ and with n going from 1 to b, or $\{(N+n)l,N(l+1)\}$ with l going from 0 to $N-2$ and with n going from 0 to b.

The question now is how to choose b to pick up the significant configurations. Let us suppose that we have fixed N and l and we are adding to the basis set the states with increasing n. We made variational calculation with k basis functions and calculated the ground state of given symmetry E_k. We add the $(k+1)$th state, obtain E_{k+1} and calculate the difference $E_{k+1}-E_k$. If this difference is less than ε, contribution of the states with fixed N and l is saturated. Addition of the further states with fixed N and l and increasing n does not improve the variational result significantly. For the triplet S and P states we took $\varepsilon=10^{-9}$, for the singlet S state we took $\varepsilon=10^{-7}$. In this way we determined b.

For $\{Ns,(N+n)s\}$ configurations of the triplet S state and $\{1s,np\}$ of the triplet P state we took $\xi_{2k}=1-1/Z$ and $\xi_{1k}=1$. In these configurations, the distinction between the "inner" and "outer" electrons is meaningful. The "inner" electron "sees" the nuclear charge and the "outer" electron "sees" the nuclear charge screened by the "inner" electron. For other configurations we took $\xi_{1k}=\xi_{2k}=1$.

Tables I and II summarize our findings about significant configurations for the S and P states, respectively. For low N the contribution of the states with small $l=0,1,2$ is dominant and we have to take large number of the excitations of the "outer" electron. As we move to larger values of N, the contribution of the states with small l saturates. The dominant contribution is shifted to the states with $l=3,4,5$. Also, as N increases the contributions of the configurations with larger n goes down. In other words, as we are moving to the higher excited states the electrons have tendency to have equal principal quantum numbers.

However, it is seen from Tables I and II that precise dependence of b on N and l that cuts the unsignificant configurations is anything but simple. Perhaps labeling of the configurations by means of the approximate quantum numbers

TABLE I. The basis set used for configuration interaction for the S states. $\{Nl,(N+n)l\}$ configurations are ordered according to the principal quantum number N of the "inner" electron. For fixed N, the orbital quantum number l runs from 0 to $N-1$. For fixed N and l the difference n between the principal quantum numbers of the "outer" and "inner" electron ranges from 0 (for the singlets) or from 1 (for the triplets) to b. b serves to cut the contribution of the states with large n that do not significantly improve the variational result. b was determined from numerical experiments, see the main text for the details.

State	Interval	b
^1S	$N<12,\ l<3$	9
	$N<12,\ l\geqslant 3$	$9-(l-2)$
	$12\leqslant N\leqslant 18$	$6-\lvert l-4\rvert$
^3S	$N\leqslant 5$	$18-N-2l$
	$6\leqslant N\leqslant 8$	$18-N-l$
	$9\leqslant N\leqslant 13$	$18-N-\lvert l-4\rvert$

as used by Herrick and Sinanoglu [15] provides the desired "selection rule."

C. Results and discussion

We first discuss accuracy of the eigenvalues and then numerical stability of the integrals. The results presented in Tables III–V show that after relatively fast convergence for small N, the convergence of CI slows down for larger N. The results were compared with those obtained in Ref. [20] with the method of the explicitly correlated functions. As expected, the result for the ground state is not impressive. It is well known that electron-electron correlation for the lowest state of two-electron atoms is very strong. Thus, the results obtained within the orbital method are relatively poor in comparison with those obtained by means of the explicitly correlated functions, see, e.g., Refs. [6,17,21,22]. The latter method has the disadvantage that its extension to the atoms with more than two electrons is very complicated. Three-electron atoms are just on the margin of feasibility [23]. The accuracy of our calculation is much better for the excited states. Our results for 2 ^3S and 2 ^3P states are better than 1 part in 10^6. Considering the simplicity of the basis set used here in comparison with that used in Ref. [20], these results

TABLE II. The same as in Table II but for the P states. The only difference is that in this case we have two kinds of configurations $\{Nl,(N+n)(l+1)\}$ and $\{(N+n)l,N(l+1)\}$.

Configurations	Interval	b
$\{Nl,(N+n)(l+1)\}$	$N=1$	15
	$N=2$	$13-2\lvert l-1\rvert$
	$N=3$	$10-2\lvert l-1\rvert$
	$4\leqslant N\leqslant 8,\ l<4$	7
	$4\leqslant N\leqslant 8,\ l\geqslant 4$	$7-(l-3)$
	$9\leqslant N\leqslant 13,\ l<7$	4
	$9\leqslant N\leqslant 13,\ l\geqslant 7$	$4-(l-6)$
$\{(N+n)l,N(l+1)\}$	$N=2$	14
	$N=3$	$13-2(l-1)$
	$4\leqslant N\leqslant 5$	7
	$6\leqslant N\leqslant 10,\ l<4$	5
	$6\leqslant N\leqslant 10,\ l\geqslant 4$	$5-(l-3)$
	$11\leqslant N\leqslant 13,\ l<7$	$5-(N-10)$
	$11\leqslant N\leqslant 13,\ l\geqslant 7$	$5-(N-10)-(l-6)$

TABLE III. Variational energy levels E_N of the ground state of helium obtained by diagonalization of the generalized eigenvalue problem (88) for given N. Order denotes the order of the truncated matrix. ΔE denotes the difference E_N-E_{N-1}. The exact value is -2.903724373 [20].

N	Order	E_N	ΔE
1	10	−2.8725067	
2	30	−2.8975136	$-0.25\ 10^{-1}$
3	60	−2.9009036	$-0.33\ 10^{-2}$
4	99	−2.9020298	$-0.11\ 10^{-2}$
5	146	−2.9025655	$-0.53\ 10^{-3}$
6	200	−2.9028682	$-0.30\ 10^{-3}$
7	260	−2.9030582	$-0.18\ 10^{-3}$
8	325	−2.9031862	$-0.12\ 10^{-3}$
9	394	−2.9032773	$-0.91\ 10^{-4}$
10	466	−2.9033447	$-0.67\ 10^{-4}$
11	540	−2.9033962	$-0.51\ 10^{-4}$
12	586	−2.9034357	$-0.39\ 10^{-4}$
13	632	−2.9034672	$-0.31\ 10^{-4}$
14	678	−2.9034922	$-0.24\ 10^{-4}$
15	724	−2.9035120	$-0.19\ 10^{-4}$
16	770	−2.9035277	$-0.15\ 10^{-4}$
17	816	−2.9035404	$-0.12\ 10^{-4}$
18	862	−2.9035508	$-0.10\ 10^{-4}$

TABLE IV. The same as in Table III, but for the 2^3S state. The exact value is -2.175229378 [20].

N	Order	E	ΔE
1	17	−2.174245506	
2	47	−2.175088716	$-0.84\ 10^{-3}$
3	86	−2.175208569	$-0.11\ 10^{-3}$
4	130	−2.175221935	$-0.13\ 10^{-4}$
5	175	−2.175225653	$-0.37\ 10^{-5}$
6	232	−2.175227182	$-0.15\ 10^{-5}$
7	288	−2.175227945	$-0.76\ 10^{-6}$
8	340	−2.175228372	$-0.42\ 10^{-6}$
9	401	−2.175228626	$-0.25\ 10^{-6}$
10	456	−2.175228790	$-0.16\ 10^{-6}$
11	502	−2.175228901	$-0.11\ 10^{-6}$
12	537	−2.175228977	$-0.75\ 10^{-7}$
13	562	−2.175229025	$-0.47\ 10^{-7}$

TABLE V. The same as in Table III, but for the 2^3P state. The exact value is −2.133164181 [20].

N	Order	E	ΔE
1	15	−2.131319860	
2	54	−2.132970321	$-0.16\ 10^{-2}$
3	106	−2.133129547	$-0.15\ 10^{-3}$
4	158	−2.133151474	$-0.21\ 10^{-4}$
5	224	−2.133157958	$-0.64\ 10^{-5}$
6	292	−2.133160583	$-0.26\ 10^{-5}$
7	368	−2.133161872	$-0.12\ 10^{-5}$
8	450	−2.133162588	$-0.71\ 10^{-6}$
9	521	−2.133163013	$-0.42\ 10^{-6}$
10	594	−2.133163291	$-0.27\ 10^{-6}$
11	672	−2.133163480	$-0.18\ 10^{-6}$
12	740	−2.133163610	$-0.12\ 10^{-6}$
13	798	−2.133163699	$-0.89\ 10^{-7}$

are good. Going to the higher excited states, the performance of the orbital method further improves, see, e.g., Ref. [4].

To improve the result achieved here it is necessary to optimize screening constants, classify the configurations according to the scheme proposed by Herrick and Sinanoglu and to extrapolate the results to infinite N. This will be discussed elsewhere.

In Table VI a few values of the repulsion integrals between $\{1s,2p\}$ configuration and the excited configurations are presented. Also presented are a few diagonal matrix elements between the highly excited configurations. These configurations are the last considered configurations for given N. The values of the integrals were calculated in the double precision and then compared with the calculation performed in quadruple precision. It is seen from Table VI that the numerical stability of the method is very high. To conclude, these preliminary results show that the algebraic method developed in this paper is sound.

VI. CONCLUSIONS

In this paper two goals were achieved. First, we have shown that conservation of the Runge-Lenz vector and the commutation relations between components of the Runge-Lenz vector and angular momentum provides recurrence relations for the radial functions of the hydrogen. Second, we have shown that these recurrence relations facilitated the numerical stability of calculations. In particular, the integrals over four radial functions were written as a linear combination of the integrals over two radial functions. Numerically stable recurrence relations for the coefficients of the linear combination were found. The integrals over two radial functions were given through numerically stable recurrence relations. The method was applied to the calculation of $1\,^1S$, $2\,^3S$, and $2\,^3P$ states of helium. The results obtained here are in agreement with the other calculations.

We would like to point out that with the methods developed in this paper the treatment of the radial degrees of freedom is neither more complicated nor less elegant than the treatment of the angular ones. We note that the only analytical tools used in the evaluation of the two electron integrals (46) were the multipole expansion (47) and the integration by parts, Eqs. (63) and (71). In the evaluation of the one-electron integrals we calculated analytically the integrals over nodeless functions (B3). The rest of the calculation was algebraic. In fact, the calculation can be carried out in a completely algebraic way [24]. By means of the recurrence relations derived in Sec. III and Appendix B, we can calculate the matrix r_{12}^2. The matrix elements of r_{12}^{-1} then can be calculated by means of the improved Newton method for square-root of the matrix [25].

Algebraic method for the calculation of the atomic integrals developed in this paper can be extended to the calculation of the oscillator strengths [20,26], Bethe logarithm [21,27] and relativistic effects [28] Since the algebraic method for the calculation of the atomic integrals keeps the numerical instabilities under control, it provides the possibility of further improvement of the atomic calculation in general. Therefore, we believe that it is of some interest.

TABLE VI. Values of the integrals $\langle k|r_{12}^{-1}|j\rangle$ as calculated in the double precision where the states $|k\rangle$ and $|j\rangle$ are the symmetry adapted states given by Eq. (89) for the triplet P states, i.e., for $L=1$ and $S=1$. The results were checked in quadruple precision. Error denotes the difference between the results obtained in double and quadruple precision.

n_{1k}	l_{1k}	ξ_{1k}	n_{2k}	l_{2k}	ξ_{2k}	n_{1j}	l_{1j}	ξ_{1j}	n_{2j}	l_{2j}	ξ_{2j}	$\langle k\|r_{12}^{-1}\|j\rangle$	Error
1	0	1	16	1	1/2	10	7	1	9	8	1	$0.900831851943034\ 10^{-4}$	$-0.19\ 10^{-17}$
1	0	1	16	1	1/2	10	8	1	10	9	1	$-0.2890615746201898\ 10^{-4}$	$0.94\ 10^{-18}$
1	0	1	16	1	1/2	12	9	1	11	10	1	$0.1831898394329932\ 10^{-4}$	$-0.16\ 10^{-17}$
1	0	1	16	1	1/2	12	9	1	12	10	1	$0.4890330421218360\ 10^{-4}$	$-0.38\ 10^{-17}$
1	0	1	16	1	1/2	13	8	1	13	9	1	$0.1977285617128401\ 10^{-3}$	$-0.68\ 10^{-17}$
10	7	1	9	8	1	10	7	1	9	8	1	17.00271743870608	$-0.11\ 10^{-13}$
10	8	1	10	9	1	10	8	1	10	9	1	19.73464697927070	$0.19\ 10^{-13}$
12	9	1	11	10	1	12	9	1	11	10	1	21.51748282351638	$-0.12\ 10^{-13}$
12	9	1	12	10	1	12	9	1	12	10	1	22.41407884446250	$-0.20\ 10^{-14}$
13	8	1	13	9	1	13	8	1	13	9	1	21.84661070151542	$066\ 10^{-14}$

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APPENDIX A

This appendix is divided into four subsections. Decomposition of the operators into the radial and angular parts is described and the algebra of the angular operators is treated. The most important results on the angular momentum are summarized. The selection rules and the calculation of nonzero matrix elements of the class of the vector operators between spherical harmonics are given. The class of the vector operators considered here is a special case of the so(3) vector operators, see, e.g., Refs. [13,29,30]. In the exposition of the representation theory of so(3) vector operators we proceed along the lines of the paper [13], though some details are different.

1. Algebra of the angular operators

Taking the dot product of $\vec{n}$ and ∇^n, we get from Eqs. (4) and (6) that

$$n_k\nabla^n_k = 0. \tag{A1}$$

The ordering in the last equation is important, since components of $\vec{n}$ and ∇^n do not commute. To get their commutation relations, let us consider the well-known commutation relation $[\nabla_j, x_k] = \delta_{jk}$ and insert Eqs. (5) and (3) into ∇_j and x_k, respectively. After simple manipulations we obtain

$$[\nabla^n_j, n_k] = \delta_{jk} - n_j n_k. \tag{A2}$$

Setting $j=k$, we get (recalling that Einstein summation convention is used)

$$[\nabla^n_k, n_k] = 2. \tag{A3}$$

Equation (A1) yields an even stronger result, namely,

$$\nabla^n_k n_k = 2. \tag{A4}$$

Further, using Eqs. (3) and (5) we obtain for the components of the angular momentum

$$L_j = -i\varepsilon_{jkl}x_k\nabla_l = -i\varepsilon_{jkl}rn_k\left(n_l\frac{\partial}{\partial r} + \frac{\nabla^n_l}{r}\right) = -i\varepsilon_{jkl}n_k\nabla^n_l. \tag{A5}$$

Here, we used the well-known theorem that the product of a symmetric tensor and an antisymmetric tensor vanishes. From the last equation it is immediately clear that the components of $\vec{L}$ depend on the angular variables only. Further, taking the dot product of the vector operator $\vec{L}$ with itself we obtain

$$L^2 = -(\nabla^n)^2. \tag{A6}$$

Here, we used Eqs. (A1), (A2), and (A4) and the identity

$$\varepsilon_{jkl}\varepsilon_{jpq} = \delta_{kp}\delta_{lq} - \delta_{kq}\delta_{lp}. \tag{A7}$$

The expression for the Laplace operator in spherical coordinates can be easily obtained from Eqs. (5), (A1), (A4), and (A6)

$$-\nabla^2 = p_r^2 + \frac{L^2}{r^2}. \tag{A8}$$

Also, it immediately follows that the Hamiltonian H in Eq. (1) commutes with the square and the third component of the angular momentum L^2 and L_3.

2. Angular momentum

Let us recall only some very important relations derived in the algebraic treatment of the angular momentum. The eigenvalues and eigenvectors of the square of angular momentum and one of its components are defined by equations

$$L^2|l,m\rangle = l(l+1)|l,m\rangle \tag{A9}$$

and

$$L_3|l,m\rangle = m|l,m\rangle. \tag{A10}$$

It is advantageous to introduce the step-up and step-down operators $L_\pm = L_1 \pm iL_2$. One can show that these operators act on the eigenstates $|l,m\rangle$ as follows:

$$L_\pm|l,m\rangle = \sqrt{(l\mp m)(l+1\pm m)}|l,m\pm 1\rangle. \tag{A11}$$

Taking the Hermitian conjugate of this equation we obtain

$$\langle l,m|L_\mp = \langle l,m\pm 1|\sqrt{(l\mp m)(l+1\pm m)}. \tag{A12}$$

The magnetic quantum number m runs from $-l$ to l by 1. For orbital motion, the values of m have to be integers. Hence, possible values of orbital quantum number l are non-negative integers. The projections of the eigenvectors $|l,m\rangle$ into the coordinate basis are called spherical harmonics $Y_{l,m}(\theta,\varphi) = \langle\vec{n}|l,m\rangle$.

3. Selection rules

Next we show that from the commutation relations of the vector operators $\vec{n}$ and ∇^n with the components of the angular momentum $\vec{L}$ we can determine the matrix elements of these operators between the spherical harmonics. To get the selection rules for the quantum number l we begin by noticing that the components of operator ∇^n_k do not mutually commute. To see this, we start from the commutation relation $[\nabla_j, \nabla_k] = 0$ and insert the decomposition (5) into ∇_k. Using Eq. (A2), we obtain after some manipulations

$$[\nabla^n_k, \nabla^n_j] = n_k\nabla^n_j - n_j\nabla^n_k. \tag{A13}$$

Using this equation together with Eqs. (A2) and (A6) we derive the commutation relations

$$[L^2, n_k] = 2(n_k - \nabla^n_k) \tag{A14}$$

and

$$[L^2,\nabla_k^n] = -2n_kL^2. \tag{A15}$$

The last two equations are operator identities. Multiplying these equations from the left by $\langle l',m'|$ and from the right by $|l,m\rangle$ and using Eq. (A9), we obtain after simple manipulations two very important equations, namely,

$$\langle l',m'|\nabla_k^n|l,m\rangle = \frac{2+l(l+1)-l'(l'+1)}{2}\langle l',m'|n_k|l,m\rangle \tag{A16}$$

and

$$(l'+l+2)(l'+l)(l'+1-l)(l'-1-l)\langle l',m'|n_k|l,m\rangle = 0. \tag{A17}$$

It follows from these two equations that the matrix elements of operators $\vec{n}$ and ∇^n among spherical harmonics vanish whenever $l' \neq l\pm 1$.

Let us now find the selection rules for the quantum number m. We start with the observation that for every vector operator $\vec{V}$ of the form (12) the commutation relations

$$[L_j,V_k] = i\varepsilon_{jkm}V_m \tag{A18}$$

holds. This follows from Eqs. (A2), (A5), and (A13). Thus, the operators $\vec{V}$ given by Eq. (12), are special cases of the so(3) vector operators, see, e.g., [13,29,30]. It follows from these equations that

$$[L_3,V_3] = 0 \tag{A19}$$

and

$$[L_3,V_\pm] = \pm V_\pm, \tag{A20}$$

where the usual notation

$$V_\pm = V_1 \pm iV_2 \tag{A21}$$

has been used. Multiplying the last two equations by $\langle l'm'|$ from the left and by $|l,m\rangle$ from the right and using Eq. (A10) we get

$$\langle l',m'|V_3|l,m\rangle = 0, m' \neq m \tag{A22}$$

and

$$\langle l',m'|V_\pm|l,m\rangle = 0, m' \neq m\pm 1. \tag{A23}$$

4. Calculation of nonzero matrix elements

The nonzero matrix elements of operator $\vec{V}$ can be evaluated by means of the commutator

$$[L_+,V_+] = 0. \tag{A24}$$

This equation follows from Eq. (A18). Further, we multiply this equation by $\langle l-1,m+1|$ from the left and by $|l,m\rangle$ from the right. Using Eqs. (A11) and (A12) to get the action of operator L_+ on spherical harmonics, we obtain

$$\frac{\langle l-1,m+1|V_+|l,m\rangle}{\langle l-1,m+2|V_+|l,m+1\rangle} = \sqrt{\frac{(l-m)(l-m-1)}{(l-m-1)(l-m-2)}}. \tag{A25}$$

Since the numerator and denominator on both sides of this equation differ by the substitution $m\rightarrow m+1$, the most general form of the matrix elements reads

$$\langle l-1,m+1|V_+|l,m\rangle = c_l\sqrt{(l-m)(l-1-m)}, \tag{A26}$$

where coefficient c_l is independent on m.

The matrix elements of operators V_3 and V_- can now easily be found. Using the last equation, the commutation relation

$$V_3 = -\frac{1}{2}[L_-,V_+] \tag{A27}$$

and Eqs. (A11) and (A12) we obtain the matrix element of operator V_3

$$\langle l-1,m|V_3|l,m\rangle = c_l\sqrt{(l-m)(l+m)}. \tag{A28}$$

Similarly, using the last equation, Eqs. (A11) and (A12) and the commutation relation

$$V_- = [L_-,V_3], \tag{A29}$$

we finally obtain

$$\langle l-1,m-1|V_-|l,m\rangle = -c_l\sqrt{(l+m-1)(l+m)}. \tag{A30}$$

The remaining nonzero matrix elements can be obtained by assuming that operator V_3 is real. Coefficient c_l is then real. Taking the Hermitian conjugate of Eqs. (A26), (A28), and (A30), we get successively

$$\langle l+1,m-1|V_-|l,m\rangle = c_{l+1}\sqrt{(l-m+2)(l-m+1)}, \tag{A31}$$

$$\langle l+1,m|V_3|l,m\rangle = c_{l+1}\sqrt{(l+1-m)(l+1+m)}, \tag{A32}$$

and

$$\langle l+1,m+1|V_+|l,m\rangle = -c_{l+1}\sqrt{(l+m+1)(l+m+2)}. \tag{A33}$$

So far, we have determined dependence of the matrix elements on the quantum number m. To determine coefficient c_l, we note that

$$\begin{aligned}(V_+V_- + V_3^2)|l,m\rangle &= [c_l^2(2l-1)(l+m) + c_{l+1}^2(l+1-m)(2l+3)]|l,m\rangle \\ &= (V^2 - i[V_1,V_2])|l,m\rangle.\end{aligned} \tag{A34}$$

The first equality follows from Eqs. (A26), (A28), and (A30)–(A33). The second equality follows from Eq. (A21) and the definition of $V^2 = V_kV_k$. Equation (A34) is an important result and it was used in the Sec. II to determine spectrum of the hydrogen atom.

APPENDIX B

In Sec. IV we showed that calculation of two-electron integrals can be reduced to calculation of one-electron integrals (76). Algebraic calculation of the overlap integrals (76) is described in this appendix. We first calculate integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$ for $L_1=L_2$. Knowing these integrals, we calculate the integrals with $L_1\neq L_2$. Again, it is important to calculate these integrals in a numerically stable way. The results obtained in this subsection can also be obtained by analytical method, see, e.g., Ref. [31].

1. Case $N_2=L_2+1$ and $L_1=L_2$

Considering Eq. (85) for $N_2=l$ yields

$$P^{l,l,l}_{N_1,l+1}(\xi_1,\xi_2)=\frac{1}{\xi_2}(N_1,l,\xi_1|l+1,l,\xi_2). \tag{B1}$$

Inserting this equation into Eq. (86) for $N_2=l+1$ we obtain the formula

$$(N_1+1,l,\xi_1|l+1,l,\xi_2)=\frac{N_1+l+1}{N_1-l}\frac{\xi_2-\xi_1}{\xi_2+\xi_1}(N_1,l,\xi_1|l+1,l,\xi_2). \tag{B2}$$

This equation is solved with the initial condition

$$(l+1,l,\xi_1|l+1,l,\xi_2)=(2^2\xi_1\xi_2)^{l+1}\frac{(2l+1)!}{(\xi_1+\xi_2)^{2l+2}}. \tag{B3}$$

This equation is obtained by inserting Eqs. (45) and (62) into Eq. (76). Having established this formula we need only to raise the quantum number N_2 from the value $l+1$ to an arbitrary value and to raise the quantum number L_2 from the value l.

2. Case $L_1=L_2$

To raise the quantum number N_2 from the value $l+1$ to an arbitrary value we start with the "analytic" formula

$$\begin{aligned}\int_0^\infty r\left(\frac{d}{dr}+\frac{1}{r}\right)&[r\widetilde{R}_{N_1,L_1}(\xi_1 r)\widetilde{R}_{N_2,L_2}(\xi_2 r)]dr\\ =0=&\int_0^\infty r\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)\widetilde{R}_{N_1,L_1}(\xi_1 r)\right]\widetilde{R}_{N_2,L_2}(\xi_2 r)dr\\ &+\int_0^\infty r\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)\widetilde{R}_{N_2,L_2}(\xi_2 r)\right]\widetilde{R}_{N_1,L_1}(\xi_1 r)dr.\end{aligned} \tag{B4}$$

Applying Eq. (64) we obtain

$$\begin{aligned}(N_1-L_1)&(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &+(N_2-L_2)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\ &-(N_2+L_2)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)=0.\end{aligned} \tag{B5}$$

Further, we consider expression

$$\int_0^\infty r2r\widetilde{R}_{N_1,L_1}(\xi_1 r)\widetilde{R}_{N_2,L_2}(\xi_2 r)dr$$

and let $2r$ act first on the function $\widetilde{R}_{N_1,L_1}(\xi_1 r)$, second on the function $\widetilde{R}_{N_2,L_2}(\xi_2 r)$. Operator $2r$ acts on these functions according to Eq. (78) as

$$\begin{aligned}\int_0^\infty & r2r\widetilde{R}_{N_1,L_1}(\xi_1 r)\widetilde{R}_{N_2,L_2}(\xi_2 r)\\ &=\frac{1}{\xi_1}[2N_1(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad-(N_1-L_1)(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)]\\ &=\frac{1}{\xi_2}[2N_2(N_1,L_1,\xi_1|N_2,L_2,\xi_2)-(N_2-L_2)(N_1,L_1,\xi_1|N_2\\ &\quad+1,L_2,\xi_2)-(N_2+L_2)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)].\end{aligned} \tag{B6}$$

Eliminating $(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of the Eqs. (B5) and (B6) we obtain

$$\begin{aligned}(N_2-L_2)&\left(\frac{1}{\xi_1}+\frac{1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\ &=2\left(-\frac{N_1}{\xi_1}+\frac{N_2}{\xi_2}\right)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad+(N_2+L_2)\left(\frac{1}{\xi_1}-\frac{1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)\\ &\quad+2\frac{N_1+L_1}{\xi_1}(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2).\end{aligned} \tag{B7}$$

Using this equation for $L_1=L_2=l$ together with Eq. (B2) we obtain all possible integrals $(N_1,l,\xi_1|N_2,l,\xi_2)$.

3. Case $L_1\neq L_2$

In general, we can assume that $L_1<L_2$, since obviously $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=(N_2,L_2,\xi_2|N_1,L_1,\xi_1)$. We raise quantum number L_2 from the value $L_2=L_1$ to the needed value as follows.

For the action of operator $r(\frac{d}{dr}+\frac{1}{r})$ on the function $\widetilde{R}_{N_2,L_2}(\xi_2 r)$ in Eq. (B4) we use Eq. (65) instead of Eq. (64). We obtain

$$\begin{aligned}(N_1-L_1)&(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &+(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\ &-(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\ &+2(L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=0.\end{aligned} \tag{B8}$$

Further, for the action of operator $2r$ on the function $\widetilde{R}_{N_2,L_2}(\xi_2 r)$ in Eq. (B6) we use Eq. (77) instead of Eq. (78). We get

$$\begin{aligned}&\frac{1}{\xi_1}[2N_1(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad -(N_1-L_1)(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad -(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)]\\ &\quad =\frac{1}{\xi_2}[-2(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\ &\qquad +(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\ &\qquad +(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)]. \qquad \text{(B9)}\end{aligned}$$

Eliminating integrals $(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of the Eqs. (B8) and (B9) we obtain

$$\begin{aligned}&2(N_1+L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad =2(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\qquad -\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\ &\qquad -2\frac{\xi_1}{\xi_2}(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\ &\qquad +\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2). \qquad \text{(B10)}\end{aligned}$$

This equation could be used for calculating the integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$ as it stands. However, it turns out that it is more advantageous to combine the last equation with Eq. (B7). Elimination of the integrals $(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of these equations yields

$$\begin{aligned}&\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\ &\quad -2\frac{\xi_1}{\xi_2}(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\ &\quad -\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\ &\quad =2\left(N_2\frac{\xi_1}{\xi_2}+L_2+1\right)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\qquad -(N_2-L_2)\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\ &\qquad +(N_2+L_2)\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2).\end{aligned}$$

$$\text{(B11)}$$

We run this equation starting from $L_2=L_1$ successively ascending the quantum number L_2 to the desired value. In particular, considering the last equation for $\xi_1=\xi_2$ leads to the equation

$$\begin{aligned}&(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_1)-(N_1,L_1,\xi_1|N_2,L_2+1,\xi_1)\\ &\quad =(N_2+L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_1)\\ &\qquad -(N_2-L_2)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_1). \qquad \text{(B12)}\end{aligned}$$

Taking into account the orthogonality of the radial functions for the same ξ, Eq. (44), we get that integrals $(N_1,L_1,\xi|N_2,L_2,\xi)$ vanish for $L_1<L_2$ and $N_1>N_2$. The nonzero integrals can be easily calculated from the last equation starting with $N_1=N_2+1$ and $L_1=L_2$.

4. Generalizations

We would like to remark that the algebraic method developed so far can also be applied to the evaluation of integrals $\int_0^\infty r^{p+1}R_{n_1,l_1}(\xi_1 r)R_{n_2,l_2}(\xi_2 r)dr$, for both positive and negative p (see also Refs. [12,32,33]). If p is positive, we use one of Eqs. (31), (35), and (36) to reduce the integrals to the form (76). If p is negative, we consider Eq. (31), Eq. (35) with l replaced by $l-1$ and Eq. (36) with l replaced by $l+1$. We eliminate $R_{n+1,l}(\xi r)$ and $R_{n-1,l}(\xi r)$ from these equations and get

$$\begin{aligned}r^{-1}R_{n,l}(\xi r)=&\frac{\xi}{l(l+1)(2l+1)}[l\sqrt{(n+l+1)(n-l-1)}\\ &\times R_{n,l+1}(\xi r)+(l+1)\sqrt{(n+l)(n-l)}\\ &\times R_{n,l-1}(\xi r)+(2l+1)nR_{n,l}(\xi r)]. \qquad \text{(B13)}\end{aligned}$$

By means of this equation we reduce the integrals of the form $\int_0^\infty r^{-|p|+1}R_{n_1,l_1}(\xi_1 r)R_{n_2,l_2}(\xi_2 r)dr$ to the integrals of the form (76).

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