S-states of helium-like ions

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ABSTRACT

A simple Mathematica (version 7) code for computing S-state energies and wave functions of two-electron (helium-like) ions is presented. The elegant technique derived from the classical papers of Pekeris (1958, 1959, 1962, 1965, 1971) [1–3] is applied. The basis functions are composed of the Laguerre functions. The method is based on the perimetric coordinates and specific properties of the Laguerre polynomials. Direct solution of the generalized eigenvalues and eigenvectors problem is used, distinct from the Pekeris works. No special subroutines were used, only built-in objects supported by Mathematica. The accuracy of the results and computation times depend on the basis size. The ground state and the lowest triplet state energies can be computed with a precision of 12 and 14 significant figures, respectively. The accuracy of the higher excited states calculations is slightly worse. The resultant wave functions have a simple analytical form, that enables calculation of expectation values for arbitrary physical operators without any difficulties. Only three natural parameters are required in the input.

The above Mathematica code is simpler than the earlier version (Liverts and Barnea, 2010 [4]). At the same time, it is faster and more accurate.

Program summary

Program title: TwoElAtomSL(SH)
Catalogue identifier: AEHY_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEHY_v1_0.html
Program obtainable from: CPC Program Library, Queen’s University, Belfast, N. Ireland
No. of lines in distributed program, including test data, etc.: 11 434
No. of bytes in distributed program, including test data, etc.: 540 063
Distribution format: tar.gz
Programming language: Mathematica 7.0
Computer: Any PC
Operating system: Any which supports Mathematica; tested under Microsoft Windows XP and Linux SUSE 11.0
RAM: \( \geq 10^9 \) bytes
Classification: 2.1, 2.2, 2.7, 2.9
Nature of problem: The Schrödinger equation for atoms (ions) with more than one electron has not been solved analytically. Approximate methods must be applied in order to obtain the wave functions or another physical attributes from quantum mechanical calculations.
Solution method: The S-wave function is expanded into a triple set of basis functions which are composed of the exponentials combined with the Laguerre polynomials in the perimetric coordinates. Using specific properties of the Laguerre polynomials, solution of the two-electron Schrödinger equation reduces to solving the generalized eigenvalues and eigenvector problem for the proper Hamiltonian. The unknown exponential parameter is determined by means of minimization of the corresponding eigenvalue (energy).
Restrictions: First, the too large length of expansion (basis size) takes the too large computation time and operative memory giving no perceptible improvement in accuracy. Second, the number of shells \( \Omega \) in the wave function expansion enables one to calculate the excited ns-states up to \( n = \Omega + 1 \) inclusive.

* This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect [http://www.sciencedirect.com/science/journal/00104655].
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1. Introduction

A large variety of techniques were developed to calculate the nonrelativistic bound energies and wave functions of two-electron atomic systems. An excellent review on this topic can be found in [5,6]. The correlation function hyperspherical harmonic method is discussed in [7]. Variational calculations of P- and D-states in H⁻, and He can be found in [8], and doubly-excited non-zero angular momentum states in helium-like systems are described in [9]. A comparison of theoretical S- and P-states of the helium isoelectronic sequence with experimental data are described, e.g., in [3,4].

Thousands of variational parameters are used in order to produce highly precise approximations only for the ground states of He-like ions (see, e.g., [10–12]). Very complicated basis functions are applied in other approaches [20,6,5,16,17,7]. A great deal of effort is devoted to the derivation of simple (compact) and accurate wave functions [13–15,18,19,6]. However, the latter present a very rough approximations giving an accuracy of about 3–4 significant figures in energies.

This paper and the corresponding Mathematica-7 code are based on the classical works of C.L. Pekeris [1–3]. The basis functions are composed of the exponentials combined with the Laguerre polynomials in the perimetric coordinates. The use of specific properties of the Laguerre polynomials enables one to obtain a very simple analytic representations for the matrix elements of the proper S-state Hamiltonian. The mentioned matrix presents a very sparse form, especially for the lowest energy states. This yields the pivotal calculation advantage for the selected basis and coordinates.

We present here two simple and short codes realizing the above techniques. The first code uses the one exponential basis and enables computation of the ground and the first two excited states (both singlet and triplet). The second code uses the two exponential basis and enables calculation of higher excited NS-states with N > 3. The accuracy of the results and computation times depends on the basis size. The ground state and the lowest triplet state energies can be computed with a precision of 12 and 14 significant figures, respectively. The accuracy of the higher excited states is slightly worse. Only three natural parameters are required as input.

The resultant wave functions have a simple analytical form, that enables one to calculate the expectation values of arbitrary physical operators without any difficulties.

2. Theoretical background

Considering only S-states, the general Hamiltonian of two electrons moving in the electric field of an infinitely heavy ion of charge Z takes the following form (see, e.g., Ref. [1]):

\[
\hat{H} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{\partial^2}{\partial (r_1 r_2)} \right) - \frac{1}{2} \left( \frac{\partial}{\partial r_1} \right)^2 - \frac{Z}{r_1} + \frac{1}{2} \left( \frac{\partial}{\partial r_2} \right)^2 - \frac{Z}{r_2} + \frac{1}{2} \left( \frac{\partial}{\partial (r_1 r_2)} \right)^2 + \frac{Z}{r_1 r_2}.
\]

Here \( r_1 \) and \( r_2 \) are the electron distances from the nucleus, and \( r_{12} \) is their mutual distance. Atomic units are used throughout this paper.

The nonrelativistic Schrödinger equation for the bound state with energy \( \epsilon \) is given by:

\[
(\hat{H} - \epsilon)\phi(r_1, r_2, r_{12}) = 0,
\]

where the simplest wave \( S \)-function can be presented in the form:

\[
\phi(r_1, r_2, r_{12}) = e^{-ar_2 - br_1} F(r_1, r_2, r_{12}).
\]

2.1. Coordinates and basis functions

Let us replace the variables \( r_1, r_2, r_{12} \) by the perimetric coordinates \( u, v, w \) defined by

\[
x = r_2 + r_{12} - r_1, \quad y = r_1 + r_{12} - r_2, \quad z = r_1 - r_{12} + r_2.
\]

These coordinates are independent, and range from 0 to \( \infty \), whereas the standard coordinates \( r_1, r_2, r_{12} \) are constrained by the triangular condition.

In these perimetric coordinates the volume element and the solution (3) become:

\[
dV = 2\pi^2 r_1 r_2 r_{12} dr_1 dr_2 dr_{12} = T(u, v, w; a, b) du dw dv, \quad T(u, v, w; a, b) = \frac{\pi^2}{4a^8 b^4 (a + b)^3} F(u, v, w).
\]

Substituting Eqs. (6)–(8) into the Schrödinger equation (2), one obtains:

\[
T(u, v, w; a, b)(\epsilon - \hat{H})\psi(u, v, w) = e^{-\frac{1}{2}(u + v + w)} \frac{\pi^2}{12a^8 b^4 (a + b)^3} \tilde{F}(u, v, w),
\]

where

\[
\tilde{F} = \xi_u d_u + \xi_v d_v + \xi_w d_w + \xi_{uw} d_{uw} + \xi_{vw} d_{vw} + \xi_{uv} d_{uv} + \xi_{vw} d_{uw} + \xi_{uw} d_{vw} + \xi_{ux} d_{ux} + \xi_{vy} d_{vy} + \xi_{yv} d_{yv} + \xi_{wx} d_{wx},
\]

\[
d_\xi = \frac{\partial}{\partial \xi}; \quad d_{\xi} = \frac{\partial^2}{\partial \xi \partial \eta} (\xi, \eta = u, v, w),
\]

\[
\xi = Z \xi_Z + \epsilon \xi_\epsilon + a^4 \xi_{50} + a^4 b^4 \xi_{41} + a^3 b^4 \xi_{32} + a^4 b^2 \xi_{23} + a^2 b^2 \xi_{22} + ab^3 \xi_{13} + ab^4 \xi_{14} + b^5 \xi_{05}.
\]

Explicit expressions for \( \xi \)-factors in Eqs. (10), (12) are presented in Table 1.

2.2. One exponential form

First, let us consider the F-function of the form:

\[
F(u, v, w) = \sum_{l,m,n=0}^{\Omega} A(l, m, n)L_l(u)L_m(v)L_n(w),
\]

where \( L_k(x) \) denote the Laguerre polynomials. The summation in Eq. (13) is performed over the shells described by the build-up value of \( \omega = l + m + n \) (\( \omega = 0, 1, \ldots, \Omega \)).
Substituting expansion (13) into the RHS of Eq. (9) and using the recurrence relations between the Laguerre polynomials, one obtains a set of linear equations for the coefficients $A(l,m,n)$ expressed in the following implicit form

$$\mathcal{R}(l, M, N) \equiv \sum_{\alpha, \beta, \gamma} C_{\alpha, \beta, \gamma}(l, M, N) A(l + \alpha, M + \beta, N + \gamma) = 0.$$  

(14)

In the latter sum the maximum number of terms equals 125 ($5^3$). However, only 57 terms, satisfying the condition $|\alpha| + |\beta| + |\gamma| < 4$, are different from zero. In the simplest case of $a = b = \sqrt{-\varepsilon}$ only 33 coefficients [1] are different from zero.

Eq. (14) is a set of linear equations for the coefficients $A(l,m,n)$,

$$\sum_{l,m,n} R(L, M, N; l, m, n) A(l, m, n) = 0,$$

(15)

where the matrix elements are given by

$$R(L, M; N; l, m) = \sum_{\alpha, \beta, \gamma} C_{\alpha, \beta, \gamma}(l, M, N) \delta_{l, l'} \delta_{M, M'} \delta_{N, N'}.$$

(16)

Here, $\delta_{\alpha, \beta}$ denotes Kronecker delta symbol. For brevity, we don’t present here the explicit form of all the 57 non-zero C-coefficients. However, one can find them in the first accomplishing Mathematica coden file.

It follows from the $r_1 = r_2$ permutational symmetry that for the wave function defined in Eqs. (8) and (13), one should put

$$a = b$$

(17)

and

$$A(l, m, n) = \pm A(m, l, n),$$

(18)

where the plus sign corresponds to the singlet (para) states and the negative sign to the triplet (ortho) states.

It should be realized that the matrix $R$ defined in Eq. (16) is a sum of two matrices

$$R = H - \varepsilon S,$$

(19)

where matrices $H$ and $S$ depend (in general) upon the exponential parameter $a = b = \delta$, whereas $\varepsilon$ is the binding energy. Thus, for a given value of $\delta$ one obtains the following generalized eigenvalue equation:

$$H A = \varepsilon S A.$$

(20)

The unknown parameter $\delta$ can be determined by minimization of the corresponding eigenvalue (see, e.g., [2,3]).

2.3. Two exponential expansion

The one exponential expansion (8), (13) can be effectively applied for computing the lowest energy $N$S-states with $N \leq 3$. For higher energy states ($N > 3$) one needs to use (at least) two-exponential expansion. In this case the wave function becomes:

$$\psi_2 = \sum_{l,m,n=0} A(l, m, n) f(l, m, n)$$

(21)

with basis functions $f(l, m, n)$ of the form:

$$f(l, m, n) = e^{-\frac{w}{2} L_n(w)} e^{\frac{w}{2} L_n(v)} I_m(v) + e^{-\frac{v'}{2} L_n(w)} e^{\frac{v'}{2} L_n(v')} I_m(v'),$$

(22)

Here

$$u' = ay, \quad v' = bx.$$  

(23)

The plus sign in Eq. (22) corresponds to singlet states and the minus sign to triplet states. Note that the one-exponential basis corresponds to the first term on the RHS of Eq. (22) under conditions (17) and (18).

It can be shown (see, e.g., [2]) that for any wave function $\psi$ presented by the expansion of the form (21), the quantity $(H - \varepsilon) \psi$ has to be orthogonal to every basis function $f(l, m, n)$. It is worth noting that the orthogonalization procedure has to be executed by means of the proper integration over the three-dimensional space with the volume element defined by Eqs. (6), (7). The orthogonalization along with the properties of the Laguerre polynomials lead to a new set of linear equation for $A(l, m, n)$.

$$\sum_{l,m,n} R_2(l, M, N; l, m, n) A(l, m, n) = 0,$$

(24)

where

Table 1
Explicit form of $\xi$-factors, included into Eqs. (10), (12).

$\xi_{uu} = 4a^2u[(a + b)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{uv} = 4b^2v[(a + b)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{uw} = 4(a + b)^2w[(a + b)(b^2u^2 + a^2v^2) + abw(bu + av)]$

$\xi_{vw} = -ab[(a + b)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{ww} = -ab[(a + b)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{wr} = -4b[(a + b)^2w^2 + abw(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{vq} = -4b[(a + b)^2w^2 + abw(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{r} = 4(a + b)^2[a^2v^2 + abw(bu + av)(av + bv + 2bw + 2ab^2w^2) - abw(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{v} = 4(a + b)[(a + b)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w} = 2(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)$

$\xi_{w2} = 2w[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w3} = -4vw + 4w[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w4} = -4v[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w5} = -4v[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w6} = -4v[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w7} = -4v[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$

$\xi_{w8} = -4v[(au + bw)(bu + av)(av + bv + 2bw + 2ab^2w^2)]$
Table 2
The non-relativistic 1S, 2S and 3S energies of helium atom computed by the TwoElAtomSL code. The “exact” energies are taken from [17].

<table>
<thead>
<tr>
<th>State</th>
<th>K (l)</th>
<th>444(15)</th>
<th>715(18)</th>
<th>1078(21)</th>
<th>1547(24)</th>
<th>“exact”</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S</td>
<td></td>
<td>-2.9037243776</td>
<td>-2.9037243770</td>
<td>-2.903724377026</td>
<td>-2.903724377033</td>
<td>-2.903724377034</td>
</tr>
<tr>
<td>2S</td>
<td></td>
<td>-2.1459740428</td>
<td>-2.1459740455</td>
<td>-2.14597404592</td>
<td>-2.14597404605</td>
<td>-2.14597404605</td>
</tr>
<tr>
<td>3S</td>
<td></td>
<td>-2.061264</td>
<td>-2.06127184</td>
<td>-2.061271973</td>
<td>-2.0612719870</td>
<td>-2.0612719879</td>
</tr>
</tbody>
</table>

State | K (l) | 372(15) | 615(18) | 946(21) | 1378(24) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2S</td>
<td></td>
<td>-2.175229378228</td>
<td>-2.1752293782361</td>
<td>-2.17522937823672</td>
<td>-2.17522937823679</td>
</tr>
<tr>
<td>3S</td>
<td></td>
<td>-2.0688806</td>
<td>-2.0688806720</td>
<td>-2.06888067454</td>
<td>-2.06888067472</td>
</tr>
</tbody>
</table>

Table 3
The nonrelativistic energies of helium atom computed by the TwoElAtomSH code. The “exact” NS-energies for N ≤ 10 are taken from [17], whereas the other ones (N > 10) are taken from [3].

<table>
<thead>
<tr>
<th>State</th>
<th>K (l)</th>
<th>220(9)</th>
<th>286(10)</th>
<th>364(11)</th>
<th>455(12)</th>
<th>560(13)</th>
<th>680(14)</th>
<th>“exact”</th>
</tr>
</thead>
</table>

\[
R_2(L, M, N; l, m, n) = \sum_{\alpha, \beta, \gamma=1}^{2} C_{\alpha, \beta, \gamma}(l - \alpha, m - \beta, n - \gamma) \\
\times \delta_{N, N-\gamma} \delta_{l, l-\alpha} \delta_{m, m-\beta} \\
\pm T(l, M; l - \alpha, m - \beta). 
\]

(25)

The C-coefficients were defined above, and

\[
T(l', m' ; l, m) = (-1)^{m + m'} \frac{4ab}{(b + a)^2} \left( \frac{b - a}{b + a} \right)^{l + l' + m + m'} \\
\times g(l', m) g(l, m).
\]

(26)

where

\[
g(l, m) = 2F1 \left( -l, -m; 1; \frac{-4ab}{(a - b)^2} \right)
\]

(27)

given in terms of the Gauss hypergeometric function \(2F1\).

The matrix elements (25)–(27) depend on two parameters \(a\) and \(b\). The following parameterization

\[
a = Z, \quad b = \sqrt{-2e - Z^2}
\]

(28)
giving the correct asymptotic behavior was proposed in Ref. [2]. However, significantly more exact results can be obtained if parameter \(b\) is allowed to vary [2,3]. In this paper (and in the associated Mathematica code) we apply the latter parameterization. Thus, setting \(a = Z\) and \(b = \delta\), once again one comes to the generalized eigenvalue problem, \(H_2A = \epsilon S_2A\).

(29)

The matrices \(H_2\) and \(S_2\) depend on a single parameter \(b = \delta\), which can be determined by minimizing the eigenvalue \(\epsilon\) under consideration.

3. Numerical results

The technique described above is realized in two Mathematica codes. The first code entitled “TwoElAtomSL” calculates the nonrelativistic binding energies and wave functions for 1S, 2S and 3S states (both singlet and triplet). The second code entitled “TwoElAtomSH” computes energies and wave functions for NS excited states with \(N > 3\). Some numerical results obtained with these codes are shown in Tables 2–4. The results are presented for the helium atom, because this atom of the helium isoelectronic sequence is best described in the scientific literature. Note that the given number of shells \(\Omega\), in the wave function expansion, enables one to provide the reliable calculations of the excited NS-states up to \(N = \Omega + 1\) inclusive.

The ground state and the first two excited states energies calculated by “TwoElAtomSL” are presented in Table 2 for \(\Omega = 15, 18, 21, 24\) (shown in parentheses). The corresponding orders \(K\) of matrices \(H\) and \(S\) are 444, 715, 1078, 1547 for singlet and 372, 615, 946, 1378 for triplet states, respectively. Our results are compared with the highly accurate results of Drake et al. [17], presented in the last column. It is seen, that the code can yield an energy accuracy of the order of 12 significant figures for 1S and 14 significant figures for 2S states.
The highly excited singlet and triplet states energies are presented in Table 3. The results are shown for \( \Omega = 9, 10, 11, 12, 13, 14 \) corresponding to \( K = 220, 286, 364, 455, 560, 680 \), respectively. For comparison, the accurate (45–105) energies retrieved from [17] and (115–155) energies retrieved from [3] are shown in the last columns of Table 3. One can observe, that the code “TwoElAtomSH” can provide an accuracy of 7 and 9 significant figures for the 4\(^d\)S and the 4\(^f\)S energies, respectively. The precision of the calculated states declines with increasing excitation up to 5 significant figures for the 155 state.

To demonstrate the quality of the wave functions produced by the “TwoElAtomSL” code, the expectation values of the following operators \((r_1), (r_2), (1/r_1), (1/r_2), (\delta(r_1)), (\delta(r_2))\) are displayed in Table 4 for the helium atom. The number of shells \( \Omega = 24 \) \((K = 1547)\) was used for computing the ground and the first two excited states. Both the nonrelativistic energies and the expectation values coincide with the results presented in [1, 3].

### 4. Description of the software structure and the individual software components

The theoretical background of the method needed for calculating the S-states electronic structure of a two-electron atomic systems was described in Section 2. A simple code realizing this technique was composed using Mathematica, version 7. In fact, this code encloses two program units (PU) written in three files. As it was mentioned at the beginning of the previous section, the first PU entitled “TwoElAtomSL” is intended for computing 1S, 2S and 3S binding energies and wave functions, whereas the second one entitled “TwoElAtomSH” is for the higher excited NS-states with \( N > 3 \).

The first input cell of the both PUs is written to the file (notebook) “KSI_factors”, whereas the other cells are written to the files (notebooks) “LowEst” and “HighEst” for the “TwoElAtomSL” and “TwoElAtomSH” PUs, respectively. Both PUs are divided into few (evaluable) cells, that must be executed (run) step-by-step.

Hereafter all the Mathematica objects presented in the Mathematica codes will be marked by an overline.

Cell 1 and Cell 2 are common to both PUs.

Cell 1 is intended for setting the analytic \( \xi \)-factors, described in Section 2 and presented in Table 1. The \( \xi \)-factors are placed in the list \( \text{LIFF} \).

Cell 2 is meant for setting the numerical INPUT data:

1) \( Z \) – nucleus charge (in atomic units);
2) \( \Sigma \) – singlet/triplet key. It must be positive for singlet states, and negative for triplet states;
3) \( \Omega \) – the number of shells in the wave function expansion. The basis size \( K \) (length of expansion) depends on the value of \( \Omega \).

The TwoElAtomSL PU (LowEst.nb):

Cell 3 is meant for calculation of the matrix elements of the matrix \( R \) defined by Eq. (16). First, the one-exponential parametrization (17) is given by \( a = b = \delta \). The \( C \)-coefficients defined by Eq. (14) are tentatively retrieved from the list \( \text{LIFF} \) and are placed to \( \text{CE} \) in explicit form. The resultant matrix elements are placed to the matrix \( \text{RS} \).

Cell 4 serves finally for computing the binding energies and the \( A \)-coefficients of the wave function (13). To this end, the eigenvalues of Eq. (20) are integrated in \( \text{FM} \) presenting a function of parameter \( \delta \) and the number of the required eigenvalue. According to Eq. (20) the matrices \( H \) and \( S \) are extracted from \( \text{RS} \) and are placed in \( \text{SparseArray \text{PO} and PT} \), respectively. Parameter \( \delta \) is determined by minimization of the function \( \text{FM} \). Notice that for the presented \( \text{FM} \) only Method \( \rightarrow \) “PrincipalAxis” can provide a rapid execution (without any problems) of the built-in Mathematica FindMinimum program. As a starting point for minimization \( \text{FM} \) corresponding to the given \( \Omega \), the value of \( \delta (\Omega - 2) \) calculated previously is used. For the obtained value of \( \delta \) corresponding to the minimum of the given eigenvalue, the proper \( A \)-eigenvectors are calculated. The resultant binding energies (\( \epsilon \)-eigenvalues), exponential parameters \( \delta \) and the \( A \)-coefficients (eigenvectors) are located in arrays \( \text{EN}, \text{DEL}, n \) and \( \text{e\nu} \), respectively. The values of \( \epsilon \) and \( \delta \) are printed.

Cell 5 serves for calculating and printing the expectation values of various operators. The proper integration is performed in the perimetric coordinate system. The inverse transformation for (4), (5) is applied. The three-dimensional integrals required for obtaining the expectation values of \( r_1, r_2, 1/r_1, 1/r_2 \) operators are calculated analytically, whereas the one-dimensional integrals required for obtaining the expectation values of \( \delta(r_1) \) and \( \delta(r_2) \) operators are computed numerically.

The TwoElAtomSH PU (HighEst.nb):

Cell 3 is meant for calculation of the matrix elements of the matrix \( R \) defined by Eqs. (25)–(27). First, the two-exponential parametrization is given by \( a = Z; b = \delta \). \( C \)-coefficients defined by Eq. (14) are tentatively retrieved from the list \( \text{LIFF} \) and are placed to \( \text{CE} \) in explicit form. The resultant matrix elements are placed to the matrix \( \text{RS} \).

Cell 4 serves for extracting the individual matrices \( H_2 \) and \( S_2 \) from \( \text{R} \). The resultant matrix elements are located in \( \text{PO} \) and \( \text{PT} \), respectively.

Cell 4a is an additional one. It provides normalization of the basis set. This cell must be executed in case of appearing the Mathematica problems when running Cell 5 and Cell 6 (what is usually happened at large \( \Omega > 12 \)). A large amount of operative memory and calculation time are requested for execution of this cell and the following cells. Therefore, Cell 4a must be executed only when needed. Once Cell 4a will be executed, Cell 5 and Cell 6 must be recalculated.

Cell 5 is intended for computing the bound energy and the \( A \)-coefficients of the wave function expansion (21)–(23) for the 4S-state. To this end, the eigenvalues of Eq. (29) are integrated in \( \text{FM} \) presenting a function of parameter \( \delta \) and the number of the required eigenvalue. The final value of \( \text{FM} \)-function presents eigenvalue, which can be selected by two ways: “1” is a selection on a number of eigenvalue, whereas “ii” presents a selection of eigenvalue which is nearest to the one computed on the previous step. For this cell, “i”-way is used as an initial value, and then only “ii”-way is applied. Parameter \( \delta \) is determined by minimization of the function \( \text{FM} \). One uses option Method \( \rightarrow \) “PrincipalAxis.”

4.3. PUs related to the three-dimensional integrals required for obtaining the expectation values of \( \delta(r_1) \) and \( \delta(r_2) \) operators are computed numerically.
for minimization with \texttt{FindMinimum} program. As a starting point for minimization \( FM \) corresponding to the given \( \mathcal{C} \), the value of \( \delta(\mathcal{C} - 1) \) calculated on the previous step is used. For the final value of \( \delta \) corresponding to the minimum of the 4S-eigenvalue the proper \( A \)-eigenvector is calculated. The resultant 4S-energy, exponential parameters \( \delta \) and the \( A \)-coefficients are located in \( EN[4], DEL[4] \) and \( eiv[4] \), respectively. The values of \( \epsilon \) and \( \delta \) are printed.

Cell 6 serves for calculating the binding energies and the \( A \)-coefficients of the wave function expansion (21)–(23) for the \( NS \)-states with \( N > 4 \). Parameter \( \delta \) is determined by minimization of the function \( FM \). The value of \( \delta \) obtained for \( NS \)-state is used as a base of starting point of the energy minimization for \((N+1)S\)-state. In order to calculate 5S, 6S and 7S states one uses “ii”-way (see, description to Cell 5). For higher states one uses “i”-way and extrapolated values of starting points of minimization (to cut the computation time down). For the obtained value of \( \delta \) corresponding to the minimum of the given eigenvalue, the proper \( A \)-eigenvectors are calculated. The resultant binding energies, parameters \( \delta \) and the \( A \)-coefficients are placed to the proper positions in arrays \( EN, DEL \) and \( eiv \), respectively. The values of \( \epsilon \) and \( \delta \) are printed.

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References

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