Matrix mechanics for actual atoms and molecules

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Abstract

Matrix mechanics is developed to describe the bound state spectra in few- and many-electron atoms, ions and molecules. Our method is based on the matrix factorization of many-electron (or many-particle) Coulomb Hamiltonians which are written in hyperspherical coordinates. As follows from the results of our study the bound state spectra of many-electron (or many-particle) Coulomb Hamiltonians always have the ‘ladder’ structure and this fundamental fact can be used to determine and investigate the bound states in various few- and many-body Coulomb systems.

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I. INTRODUCTION

In this communication we develop the matrix mechanics of the actual, i.e. few- and many-electron, atoms, ions and molecular systems. This approach is, in fact, a very powerful method for analysis of various few- and many-electron Coulomb systems which can successfully be applied to describe the bound state spectra in different atoms, ions and even molecules. Our approach is a new step in the development of Matrix Mechanics \[1\] which was originally created by Heisenberg, Born and Jordan as the first version of Quantum Mechanics \[2, 3\]. Briefly, we want to show how the old version of matrix mechanics can be modified to the new level and can be used as an effective tool for solving numerous problems in modern atomic physics.

Our main goal in this study is to show that the Coulomb Hamiltonian of an arbitrary atom which contain \(N_e\)–bound electrons is always factorized, i.e. it is represented in the form of a product of the two differential operators of the first order. This fundamental fact is directly related to the internal structure of the Coulomb Hamiltonians (the so-called ladder structure) and substantially simplifies analysis of the bound state spectra in few- and many-electron atoms and ions and can be used to perform more accurate numerical computations of the bound states. In particular, by using the method of matrix factorization we can determine the energies and wave functions of an arbitrary bound state in many-electron atoms and ions, including excited and highly excited bound states. The same procedure can also be used for molecules and for other many-particle Coulomb systems.

First, let us consider the one-electron hydrogen atom and/or hydrogen-like ions, i.e. atomic systems which contain one bound electron and one positively charged nucleus. To simplify our analysis in this study we shall assume that all atomic nuclei mentioned below are infinitely heavy. Furthermore, everywhere below we shall apply the atomic system of units. In these units \(\hbar = 1, |e| = 1\) and \(m_e = 1\), where \(\hbar = \frac{\hbar}{2\pi}\) is the reduced Planck constant, \(m_e\) is the electron mass and \(e\) is the electric charge of electron (a negative value). In atomic units the Hamiltonian of one-electron atoms/ions is written in the form

\[
H = - \frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{r^2} \right] - \frac{Qe^2}{r} = - \frac{1}{2} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{L^2}{r^2} \right] - \frac{Q}{r}
\]

where \(Qe = Q\) is the electric charge of the atomic nucleus and \(L\) is the operator of the angular moment of the atom which coincides with the total angular momentum of the bound atomic
electrons. To determine the bound states in the hydrogen atom and hydrogen-like ions we need to solve the corresponding Schrödinger equation \( H\Psi = E\Psi \), where the operator \( H \) is the Hamiltonian, Eq.(11), \( \Psi \) is the unknown wave function and \( E \) is the eigenvalue of \( H \) which is the total energy of the bound state, i.e. \( E < 0 \). As is well known (see, e.g., [4], [5]) the total wave function of an arbitrary bound state of the hydrogen atom is represented as a product of the radial part of the total wave function \( \psi_{n\ell}(r) \) and the corresponding spherical harmonic(s) \( Y_{\ell m}(\theta, \phi) \), i.e. \( \Psi_{n\ell m}(r, \theta, \phi) = \psi_{n\ell}(r)Y_{\ell m}(\theta, \phi) \), where \( Y_{\ell m}(\theta, \phi) \) are the eigenfunctions of the \( L^2 \) operator, i.e. \( L^2Y_{\ell m}(\theta, \phi) = \ell(\ell + 1)Y_{\ell m}(\theta, \phi) \).

Here and everywhere below the notations \( \theta \) and \( \phi \) stand for the spherical coordinates of the bound electron, while \( r \) is the electron-proton distance which coincides with the radial spherical coordinate. The integer numbers \( n, \ell \) and \( m \) are called the principal quantum number, angular quantum number and magnetic quantum number, respectively. For one-electron atomic systems all these quantum numbers are the ‘good’ (or conserving) quantum numbers. Note also that the following inequalities are always obeyed for these quantum numbers: \( \ell \leq n - 1 \) and \( |m| \leq \ell \).

In the basis of spherical harmonics \( Y_{\ell m}(\theta, \phi) \) the Hamiltonian, Eq.(11), takes the form

\[
H(r) = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{\ell(\ell + 1)}{2r^2} - \frac{Q}{r} = \delta_{\ell,\ell_1} \delta_{m,m_1} \left\{ -\frac{1}{2} \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right] + \frac{\ell(\ell + 1)}{2r^2} - \frac{Q}{r} \right\}
\]

where \( \ell \) is the angular moment of the bound electron (\( \ell \geq 0 \)) which coincides (for one-electron atoms/ions) with the angular momentum of the whole atom \( L \). Note that the Hamiltonian, Eq.(2) is a differential operator of the second order upon the radial variable \( r \). On the other hand, the Hamiltonian \( H(r) \) is a diagonal matrix in terms of the \( \ell \) and \( m \) (or \( |m| \)) indeces each of which is a conserving quantum number. The explicit solution of the Schrödinger equation \( H\psi = E\psi \) for the bound states of the hydrogen atom and hydrogen-like ions leads to the following formula (Bohr’s formula) for the energy spectrum

\[
E_n = -\frac{m_e Q^2 e^4}{2\hbar^2 n^2} = -\frac{Q^2}{2n^2} = -\frac{Q^2}{2(n_r + \ell + 1)^2}
\]

where \( n_r \) is the radial quantum number which is a non-negative integer and varies between 0 and \( n - \ell - 1 \) and \( n \) is the principal quantum number. The numerical value of \( n_r \) coincides with the number of zeros in the radial part of the wave function \( \psi_{n\ell}(r) \). Furthermore, the radial part of the total wave function \( \psi_{n\ell}(r) \) equals to the product of some positive power of \( r \), Laguerre polynomial of \( r \) and a radial exponent. In numerous textbooks this results
is derived by using a special form of the radial wave function $\psi_{n\ell}(r)$ (see, e.g., [3]). Then the original differential equation is reduced to the corresponding differential equation for the hypergeometric function $\,_{2}F_{1}(a, b; c; r)$ which must have a finite number of terms, or, in other words, to be a polynomial. This is the standard procedure which have been described in many textbooks. However, there is another procedure which can be applied to determine the bound state spectrum, i.e. the total energies and wave functions, of the hydrogen atom and hydrogen-like ions. This procedure is more elegant, physically transparent and based on the internal structure of the Coulomb Hamiltonian (see, e.g., [1]). We describe this procedure in the next Section.

II. FACTORIZATION METHOD FOR ONE-ELECTRON ATOM/ION

This Section is intended merely to summarize the central facts about the factorization method that are needed in Sections IV - V below. Another aim of this Section is to fix the notation. Now, consider the matrix of the Hamiltonian $H$, Eq.(1), in the basis of spherical harmonics, i.e. the matrix $\langle Y_{\ell m}(\theta, \phi) \mid H \mid Y_{\ell_1 m_1}(\theta, \phi) \rangle = \delta_{\ell,\ell_1}\delta_{m,m_1}\hat{H}_{\ell,m}(r) = H(r)$ which is a diagonal matrix in the $\ell$ and $m$ indices. On the other hand, each matrix element of this matrix is a differential operator of the radial variable $r$, i.e. $\hat{H}_{\ell,m}(r)$. Since the both $\ell$ and $m$ quantum numbers are the conserving (or ‘good’) quantum numbers, then we can replace the corresponding matrix notation $\hat{H}_{\ell,m}(r)$ by a simple operator notation, i.e., $\hat{H}_{\ell,m}(r) = H(r)$ (see, Eq.(2)). Our goal in this Section is to find all eigenvalues of this radial operator $H(r)$, Eq.(2). For these purposes we shall apply the factorization method developed for the differential operators of the second order. This method was well described in a number of books and textbooks (see, e.g., [1], [6] and references therein). Below, we assume that the reader is acquainted with the factorization method and its applications to one-electron atomic systems (see, e.g., [1] and references therein).

The method of matrix factorization (see, e.g., [1]) is based on the existence of a set of the first-order differential operators $\Theta_{n}(r)$ (where $n = 1, 2, \ldots$) and their adjoint operators $\Theta_{n}^{*}(r)$. The $\Theta_{n}(r)$ operators are written in the form

$$\Theta_{n}(r) = \frac{1}{\sqrt{2}}[-\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) + \beta_{n} \frac{r}{r} + \alpha_{n}]$$

(4)
In respect to this definition the adjoint operators are

\[ \Theta_n^*(r) = \frac{1}{\sqrt{2}} \left[ \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) + \frac{\beta_n}{r} + \alpha_n \right] \]  

(5)

The real parameters \( \beta_n \) and \( \alpha_n \) in operators defined by Eqs.(4) - (5) must be chosen to obey the two fundamental conditions of the factorization method. First, the Hamiltonian \( H(r) \), Eq.(2), must be represented in the form

\[ H = \Theta_1^*(r) \Theta_1(r) + a_1 \]  

(6)

where \( H \) is the Coulomb Hamiltonian, Eq.(2), of the one-electron hydrogen atom. Second, there is an infinite, in principle, chain of relations between the \( \Theta_n(r) \), \( \Theta_n^*(r) \), \( \Theta_{n+1}(r) \) and \( \Theta_{n+1}(r) \) operators:

\[ \Theta_n(r) \Theta_n^*(r) + a_n = H_{n+1} = \Theta_{n+1}^*(r) \Theta_{n+1}(r) + a_{n+1} \]  

(7)

where \( H_{n+1} \) is the \( n \)-excited Hamiltonian (or \( n \)-times excited Hamiltonian, where \( n \geq 1 \)) of the original problem. In this notation we have to assume that \( H_1 = H \). The equations, Eqs.(6) - (7), and their role in the factorization method are discussed in detail in [1]. In this study we do not want to repeat that description. Instead, we note that from Eq.(6) and explicit formulas, Eqs.(4) and (5), written for \( n = 1 \), one finds three following equations for the \( \beta_1, \alpha_1 \) and \( a_1 \) parameters

\[ \beta_1(\beta_1 - 1) = \ell(\ell + 1) \ , \quad \alpha_1 \beta_1 + \beta_1 \alpha_1 = 2\beta_1 \alpha_1 = 2Q \ , \quad a_1 = -\frac{1}{2} \alpha_1^2 \]  

(8)

From the first equation we obtain \( \beta_1 = \ell + 1 \). Another solution which corresponds to the \( \beta_1 = -\ell \) value cannot be accepted, since it produces the wave function which is singular at the radial origin, i.e. at \( r = 0 \). Such solutions have no physical sense for the Coulomb two-body problem. By using the relation \( \beta_1 = \ell + 1 \) we determine the parameter \( \alpha_1 \): \( \alpha_1 = \frac{Q}{\ell+1} \). Then from Eq.(8) one finds that \( a_1 = -\frac{Q^2}{2(\ell+1)^2} \). This expression for the parameter \( a_1 \) exactly coincides with total energy of the lowest bound state in a series of bound states with the angular momentum \( \ell \).

Analogously, by substituting the expressions, Eqs.(4) - (5), into the formula for the \( H_{n+1} \) Hamiltonian, Eq.(7), we obtain the following equations for the \( \alpha_n, \beta_n, \alpha_{n+1}, \beta_{n+1} \) and \( a_{n+1} \) values

\[ \beta_{n+1}(\beta_{n+1} - 1) = \beta_n(\beta_n + 1) \ , \quad 2\alpha_{n+1} \beta_{n+1} = 2Q = 2\alpha_n \beta_n \ , \quad a_{n+1} = -\frac{1}{2} \alpha_{n+1}^2 \]  

(9)
From these equations one finds that \( \beta_{n+1} = \beta_n + 1 = \ldots = \beta_1 + n = n + \ell + 1 \), \( \alpha_{n+1} = \frac{Q}{n+\ell+1} \) and \( a_{n+1} = -\frac{1}{2}a_{n+1}^2 = -\frac{Q^2}{2(n+\ell+1)^2} \). This value of \( a_{n+1} \) exactly coincides with the total energy of the \( n \)-th excited bound state \( (E_{n+1}) \) in the series of bound states with the given value of \( \ell \). In other words, by using this simple method one can reproduce the bound state spectra for the series of bound states with arbitrary \( \ell \) (angular momentum). It follows from here that the factorization method also produces the whole bound state spectrum of the hydrogen atom which contains the bound states with different values of angular momentum \( \ell \) (\( \ell \geq 0 \)).

Now, let us consider the energy functional \( E(\Psi) = E_1(\Psi) \) (see, e.g., [7]), where \( \Psi = \Psi(r) \) is the trial function, and the Hamiltonian \( H \) is represented in the form of Eq.(6)

\[
E(\Psi) = \frac{\langle \Psi \mid H \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} = \frac{\langle \Psi \mid \Theta_1^*(r)\Theta_1(r) \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} + a_1 = \frac{\langle \Theta_1(r)\Psi \mid \Theta_1(r)\Psi \rangle}{\langle \Psi \mid \Psi \rangle} + a_1 \quad (10)
\]

where \( a_1 \) is some negative number which is uniformly defined by \( \Psi \). Since the first term in the right-hand side of this equation is always positive, then it follows from Eq.(10) that \( \min_{\Psi} E(\Psi) = a_1 \) and such a minimum is reached on the function \( \Psi \) which is defined by the equation \( \Theta_1(r)\Psi(r) = 0 \). Thus, we have found the equation which allows one to obtain the ground state wave function \( \Psi_1(r) \) of an arbitrary one-electron atom and/or ion. At the next step we consider the subspace of functions \( \Phi \) which are represented in the form \( \Phi(r) = \Theta_1^*(r)\Psi(r) \), where the function \( \Psi \) is an arbitrary radial function defined in the \( L^2(0 \leq r < \infty) \) space. It is clear any of these functions is orthogonal to the ground state wave function \( \Psi_1(r) \), since

\[
\langle \Theta_1^*(r)\Psi(r) \mid \Psi_1(r) \rangle = \langle \Psi(r) \mid \Theta_1(r)\Psi_1(r) \rangle = 0.
\]

This means that we are dealing with the subspace of the trial functions which are represented in the form \( \Phi(r) = \Theta_1^*(r)\Psi(r) \) and all these functions \( \Phi(r) \) are orthogonal to the ground state wave function \( \Psi_1(r) \).

For the \( \Phi(r) \) functions we can investigate the following energy functional

\[
F(\Phi, \Psi) = F(\Psi) = \frac{\langle \Phi \mid \Phi \rangle}{\langle \Psi \mid \Psi \rangle} = \frac{\langle \Theta_1^*(r)\Psi \mid \Theta_1^*(r)\Psi \rangle}{\langle \Psi \mid \Psi \rangle} + a_1 \quad (11)
\]

By using the equality, Eq.(7), one can reduce this functional to the form

\[
F(\Psi) = \frac{\langle \Psi \mid \Theta_2^*(r)\Theta_2(r) \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} + a_2 = \frac{\langle \Theta_2(r)\Psi \mid \Theta_2(r) \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} + a_2 = E_2(\Psi) \quad (12)
\]

where \( E_2 \) is the variational energy of the first excited state of the hydrogen atom and \( a_2 \) is a real negative number. It is clear that the minimum of the functional \( F(\Psi) = E_2(\Psi) \), Eq.(12), equals to the \( a_2 \) value which coincides with the total energy of the first excited
state. The corresponding eigenfunction is defined by the equations: \( \Theta_2(r) | \Psi \rangle = 0 \) and \( \Theta_1(r) | \Psi \rangle \neq 0 \). Note that our trial functions used in Eq. (12) are already ‘correct’ trial functions, since they do not have any non-zero component which is proportional to the ground state wave function \( \Psi_1 \). Briefly, we can say that the minimum of the ‘excited’ energy functional equals \( a_2 \), Eq. (12), while the corresponding wave functions are obtained from the equations \( \Theta_2(r) | \Psi \rangle = 0 \).

Then we can repeat this procedure by considering the non-zero functions represented in the form \( \Theta_2^*(r) \Phi(r) = \Theta_2^*(r) \Theta_1^*(r) \Psi(r) \), where the function \( \Phi(r) \) is an arbitrary, in principle, radial function defined in the \( L^2(0 \leq r < \infty) \) space. Then, with the help of Eqs. (7) and (9) the whole process can be repeated as many times as needed to determine all energies of the bound states and their wave functions. The explicit form of the ground state wave function for one-electron atom/ion with our values of \( \beta_1 \) and \( \alpha_1 \) is \( \Psi_1(r) = Cr^\ell \exp(-\frac{Q}{\ell+1}r) \) where \( C \) is the normalization constant. This function is the well known exact wave function of the lowest (by the energy) state in the series of bound states with the given value of angular momentum \( \ell \) (see, e.g., [6]). In general, the radial wave function \( \Psi_n \) of the \( n \)-excited state can be determined from the equation \( \Theta_n(r) \Psi_n(r) = 0 \). Such a wave function must be orthogonal to the corresponding radial wave functions \( \Psi_{n-1}(r), \Psi_{n-2}(r), \ldots, \Psi_1(r) \) of all lower bound states. This means that we can consider the radial functions \( \Psi_n(r), \Psi_{n-1}(r), \ldots, \Psi_1(r) \) as a ‘basis’ in the \( n \)-dimensional subspace in the \( L^2(0 \leq r < \infty) \) space of the radial functions. As is well known such a basis in \( n \)-dimensional space can be orthogonalized by using a simple procedure which described in detail in many textbooks (see, e.g., [8], [9]). After orthogonalization we obtain the system of unit-norm radial functions which exactly coincide with the known radial functions of the hydrogenic systems (see, e.g., [5], [10]).

III. METHOD OF HYPERSPHERICAL HARMONICS

This and two following Sections are the central part of our study, since here we generalize the factorization method to the new level in order to include applications to various few- and many-electron atoms and ions, or, in other words, to many-particle Coulomb systems. Let \( N_e \) be the total number of bound electrons in such an atomic system. The approach described in the previous Section works only for one-electron atomic systems, i.e. for \( N_e = 1 \). For atomic systems which contain two, three, and/or more bound electrons we need to develop the new
approach and introduce a convenient system of new notations. First, it is clear that the total number of spatial variables in the case of many-electron atoms is substantially larger than three and we need to use more variables to designate all electron’s spatial coordinates. This problem is solved below by introducing the complete set of $3N_e$ electron hyperspherical coordinates. There are also $N_e$ electron spin coordinates which are combined in the total electron spin $S$ (or $S(S+1)$ value) and its $z-$projection $S_z$ (see below). Second, it is also a priori clear that the complete sets of conserving quantum numbers (or sets of ‘good’ quantum numbers) are substantially different for one- and few-electron atomic systems. In particular, the angular momentum of any single bound electron $\ell_i$, where $i = 1, 2, \ldots, N_e$, in many-electron atoms is not conserved. However, the vector-sum of the angular momenta of all bound electrons $\mathbf{L} = \vec{\ell}_1 + \vec{\ell}_2 + \ldots + \vec{\ell}_{N_e}$ is conserved. Analogously, for a single atomic electron the projection of its angular moment at $z-$axis, i.e. $\ell_{z_i} (= m_i)$ value, is not conserved, while the sum $L_z = \ell_{1,z} + \ell_{2,z} + \ldots + \ell_{N_e,z} = m_{1,z} + m_{2,z} + \ldots + m_{N_e,z} = M$ is a conserving (or good) quantum number which is often called the magnetic quantum number $M$. In general, for an arbitrary bound state in many-electron, non-relativistic atom/ion one finds the following set of conserving quantum numbers $L, M$ and $\pi$, where $\pi = (-1)^{\ell_1+\ell_2+\ldots+\ell_{N_e}}$ is the spatial parity of the atomic wave function, or spatial parity of the bound state. In addition to these three quantum numbers in any isolated atomic system with bound electrons one finds the two additional quantum numbers which are always conserved: (1) the total electron spin $S$ (or $S(S+1)$), and (2) the projection of the total electron spin $\mathbf{S}$ on the $z-$axis which is designated below as $S_z$. The set of these five integer and semi-integer numbers $[L, M, S, S_z, \pi]$ uniformly defines one series of bound atomic states which is usually called the atomic term (for more details, see, e.g., [10]).

In atomic physics the hyperspherical coordinates were introduced by Fock in 1954 [11] when he investigated the bound state wave function of the ground $1^1S$–state in the two-electron He atom. Later these coordinates were used in accurate computations of the different bound states of the He atom [12]. Since the middle of 1960’s the hyperspherical coordinates have extensively been used in nuclear and hyper-nuclear few-body problems. It was found that such coordinates are appropriate to describe various few-body systems which are close to their dissociation threshold(s). In 1974 Knirk [13] re-introduced the new set of hyperspherical coordinates in atomic and molecular physics. The choice of the hyperspherical coordinates in atomic problems with $N_e$–bound electrons made by Knirk was different.
from that used earlier by Fock [11]. We have found that the definition of the hyperspherical
coordinates proposed by Knirk (see Section II of his paper [13]) is more convenient and
appropriate for various atomic problems.

In this study, we shall use the same hyperspherical coordinates which exactly coincide
with such coordinates defined in [13]. In particular, the angular (or spherical) coordinates
of each electron are designated below as \( \omega_i = (\theta_i, \phi_i) \), where \( i = 1, 2, \ldots, N_e \). The radial
variables of each electron \( r_i \) are defined exactly as in Eq.(2.1) from [13] and hyper-radius \( r \)
coincides with the expression given in Eq.(2.3) from [13]. In other words, we can write for
the Cartesian coordinates of each electron

\[
x_i = r_i \sin \theta_i \cos \phi_i, \quad y_i = r_i \sin \theta_i \sin \phi_i, \quad z_i = r_i \cos \theta_i,
\]

where \( i = 1, 2, \ldots, N_e \), while \((x_i, y_i, z_i)\) are the Cartesian coordinates of the \( i \)-th electron
and \( r_i = \sqrt{x_i^2 + y_i^2 + z_i^2} \) is the spherical radial coordinate of this electron. It is clear that
\( \vec{r}_i = Y_{\ell m}(\theta_j, \phi_j) = -\Delta_i Y_{\ell m}(\theta_j, \phi_j) = \delta_{ij} \ell(\ell + 1)Y_{\ell m}(\theta_i, \phi_i) \), where \( \ell^2_i \)
is the square of the ordinary momentum operator of the particle \( i \).

Now, we can define the atomic hyper-radius \( r = \sqrt{\sum_{i=1}^{N_e} r_i^2} \) and \((N_e - 1)\) hyperspherical
angles \( \eta_2, \eta_3, \ldots, \eta_{3N_e-1} \) which are defined by the following relations

\[
r_{N_e} = r \cos \eta_{N_e}, \quad r_{N_e-1} = r \sin \eta_{N_e} \cos \eta_{N_e-1}, \quad r_{N_e-2} = r \sin \eta_{N_e} \sin \eta_{N_e-1} \cos \eta_{N_e-2}, \ldots,
\]

\[
r_2 = r \sin \eta_{N_e} \sin \eta_{N_e-1} \ldots \sin \eta_3 \cos \eta_2, \quad r_1 = r \sin \eta_{N_e} \sin \eta_{N_e-1} \ldots \sin \eta_3 \sin \eta_2
\]

The set of \((3N_e - 1)\) angular variables (compact variables) is designated below by the letter
\( \Omega \), i.e. \( \Omega = (\eta_2, \eta_3, \ldots, \eta_{N_e}, \omega_1, \omega_2, \ldots, \omega_{N_e}) \). Analogously, the partial set of \((3j - 1)\)-
angular variables is designated below by the letters \( \Omega_j \) \( (= \eta_2, \eta_3, \ldots, \eta_j, \omega_1, \omega_2, \ldots, \omega_j) \) for
\( j = 2, 3, \ldots, N_e \) and \( \Omega_{N_e} = \Omega \). These angular variables describe all angular configurations in
the cluster of \( j \) bound electrons. The square of the generalized angular momentum operator
for the cluster of \( j \) bound particles/electrons is defined by the following recursive relation

\[
\Lambda_j^2(\Omega_j) = -\frac{\partial^2}{\partial \eta_j^2} - \frac{(3j - 4) \cos^2 \eta_j - 2 \sin^2 \eta_j}{\sin \eta_j \cos \eta_j} \frac{\partial}{\partial \eta_j} + \Lambda_{j-1}^2(\Omega_{j-1}) \frac{\sin^2 \eta_j}{\cos^2 \eta_j} + \ell_j^2
\]

with the following ‘initial’ condition: \( \Lambda_1^2(\Omega_1) = \ell_1^2(\omega_1) \).

The \( 3N_e \) dimensional ‘total’ Laplacian has a very simple form in the hyperspherical
coordinates

\[
\nabla_{N_e}^2 = \sum_{i=1}^{N_e} \nabla_i^2 = \frac{\partial^2}{\partial r^2} + \frac{3N_e - 1}{r} \frac{\partial}{\partial r} - \frac{\Lambda_{N_e}^2(\Omega)}{r^2}
\]
This term is proportional to the kinetic energy of an atom/ion which contains \( N_e \) bound electrons (see below). The definition of the hyperspherical coordinates is completed by specifying the volume element in this coordinates \( d\tau = r^{3N_e-1}drd\Omega \), where \( d\Omega \) is the differential surface area on the \( 3N_e \)-dimensional hypersphere, i.e.

\[
d\Omega = \prod_{j=2}^{N_e} (\cos^2 \eta_j \sin^{3j-4} \eta_j d\eta_j) \prod_{i=1}^{N_e} (\sin \theta_i d\omega_i) = \prod_{j=2}^{N_e} (\cos^2 \eta_j \sin^{3j-4} \eta_j d\eta_j) \prod_{i=1}^{N_e} (\sin \theta_i d\theta_i d\phi_i) \quad (17)
\]

More detail description of the hyperspherical coordinates and analysis of their properties can be found, e.g., in \[13\] and in a large number of papers, books and textbooks on the method of hyperspherical harmonics and its applications to different problems from atomic, molecular and nuclear physics (see, e.g., \[14\] - \[19\] and references therein).

The \((2N_e-1)\) Laplace operators \( \Lambda_2^2(\Omega_2), \ldots, \Lambda_j^2(\Omega_j), \ldots, \Lambda_{N_e}^2(\Omega), \ell_1^2(\omega_1), \ldots, \ell_j^2(\omega_j), \ldots, \ell_{N_e}^2(\omega_{N_e}) \) depend upon different sets of angular variables. Therefore, these operators commute with each other and they have a common system of eigenfunctions. These eigenfunctions are represented in the form of products of eigenfunctions of the partial \((2N_e-1)\) Laplace operators \( \Lambda_j^2(\Omega_j) \) and \( \ell_k^2(\omega_k) \). These eigenfunctions can be chosen as the ‘natural’ basis set in the \((3N_e-1)\) angular (compact) space \( \Omega \). It is clear that each of these basis functions includes the product of the spherical harmonics of each electron, i.e. \( \mathcal{Y}(\Omega) \sim Y_{\ell_1m_1}(\theta_1, \phi_1)Y_{\ell_2m_2}(\theta_2, \phi_2) \ldots Y_{\ell_{N_e}m_{N_e}}(\theta_{N_e}, \phi_{N_e}) \). The eigenfunctions of the \( N_e-1 \) hyperspherical angles \( \eta_2, \eta_3, \ldots, \eta_{N_e} \) are the polynomial functions which are usually expressed in terms of the Jacobi (spherical) polynomials \( P_n^{(\alpha,\beta)}(x) \) \[20\], \[21\]. The products of eigenfunctions of all \((2N_e-1)\) differential operators \( \Lambda_2^2(\Omega), \ldots, \Lambda_j^2(\Omega_j), \ldots, \Lambda_{N_e}^2(\Omega), \ell_1^2(\omega_1), \ldots, \ell_{N_e}^2(\omega_{N_e}) \) mentioned above which depend upon the \( 2N_e \) angular and \( N_e-1 \) hyperangular variables are called the hyperspherical harmonics, or HH functions. In this study to designate the HH functions we use the notation \( \mathcal{Y}_{\vec{K}(b),\vec{\ell}(b),\vec{m}(b)}(\Omega) \), where \( \vec{K}(b), \vec{\ell}(b), \vec{m}(b) \) is the multi-index of the hyperspherical harmonics. The numerical value of each component of this multi-index is uniformly related with the eigenvalue(s) of the corresponding Laplace operator mentioned above.

In actual atomic computations only those hyperspherical harmonics (HH) are important which have the correct permutations symmetry between all bound electrons. In some earlier works these hyperspherical harmonics were called the ‘physical’ (or actual) HH. For atomic systems the physical harmonics can be constructed, e.g., with the use of the projection operators \( P_{LM\pi}^{SSz} \) for the given atomic term \([L, M, S, S_z, \pi]\). The explicit construction of such
projectors is well described in a number of original papers. For simple atomic systems, e.g., for the two-electron atoms/ions the explicit construction of such projection operators is very simple (see, e.g., [22]). The physical hyperspherical harmonics are extensively used in various problems of few-body physics, including description of many different atomic systems (see, e.g., [18] and references therein).

IV. FACTORIZATION METHOD FOR FEW- AND MANY-ELECTRON ATOMS AND IONS

In hyperspherical coordinates the Hamiltonian of an atom which contains \( N_e \) bound electrons is written in the form \([11], [12]\) (see, also \([13]\))

\[
H(r, \Omega) = -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{3N_e - 1}{r} \frac{\partial}{\partial r} - \frac{\Lambda_{N_e}^2(\Omega)}{r^2}\right] + \frac{W(\Omega)}{r} \quad (18)
\]

where \( \Lambda_{N_e}^2(\Omega) \) is the hypermomentum of the atom, while \( W(\Omega) \) is the hyperangular part of the interaction (Coulomb) potential which includes electron-nucleus and electron-electron parts. For an atom with \( N_e \) bound electrons the electron-nucleus term contains \( N_e \) terms, while the electron-electron part includes the \( \frac{N_e(N_e-1)}{2} \) terms. Now, we can consider the matrix of the operator \( H(r, \Omega) \) in the basis of hyperspherical harmonics (or HH-basis, for short), i.e.

\[
\hat{H}_{ab}(r) = \langle \mathcal{Y}_{K(\tilde{\ell}),\tilde{\ell}(a),\tilde{m}(a)}(\Omega) \mid H(r, \Omega) \mid \mathcal{Y}_{K(\tilde{\ell}),\tilde{\ell}(b),\tilde{m}(b)}(\Omega) \rangle \quad (19)
\]

where \( \mathcal{Y}_{K(\tilde{\ell}),\tilde{\ell}(c),\tilde{m}(c)}(\Omega) \) are the physical hyperspherical harmonics (see above), \( K(\tilde{c}) = (K_1, K_2, \ldots, K_{g_K}), \tilde{\ell}(c) = (\ell_1, \ell_2, \ldots, \ell_{g_\ell}) \) and \( \tilde{m}(c) = (m_1, m_2, \ldots, m_{g_m}) \) are the multi-indices (or vector-indices) which uniformly define the hyperspherical harmonics \( \mathcal{Y}_{K(\tilde{\ell}),\tilde{\ell}(a),\tilde{m}(a)}(\Omega) \). In turn, these multi-indices of the hyperspherical harmonics are determined by the atomic state (or atomic term) considered in calculations. In actual computations the dimensions of these vector-indices \( g_K, g_\ell \) and \( g_m \) should be minimal, since all hyperspherical harmonics applied in numerical computations are the physical HH. This means that these HH have the correct permutation symmetry, or, in other words, correct symmetry in respect to the required permutations of all electron indices. For instance, the hyperspherical harmonics which are needed in bound state calculations of the singlet \( ^1S(L = 0) \)–states of the helium atom are written in the form \( |K, \ell, \ell\rangle = |K, \ell\rangle \), where \( K = 0, 2, 4, \ldots, 2n \) is their
hypermomentum (index), while $\ell \geq 0$ (and $\ell \leq \frac{K}{2}$) is the second index (more details can be found in [22]). In other words, for this atomic system each physical HH is designated by the two-component multi-index $(K, \ell)$, i.e. in the notations introduced above one finds $g_K = 1, g_{\ell} = 1$ and $m_{g_{\ell}} = 0$. Below, we shall designate the hyperspherical matrix of the Hamiltonian $\hat{H}_{ab}(r)$ by using the same notation $H$, or $H(r)$ (as we did in the second Section). It should be mentioned that $H(r)$ is the differential operator in respect to the hyper-radius $r$ of the second order. The explicit form of the $H(r)$ Hamiltonian operator is

$$H(r, \Omega) = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r^2} + \frac{3N_e - 1}{r} \frac{\partial}{\partial r} - \hat{K}(\hat{K} + 3N_e - 2) \right] + \hat{W}$$

(20)

where $\hat{K}$ is the matrix of hypermomentum which is diagonal the basis of ‘physical’ HH, or in $K$–representation for short.

In our earlier study [17] we have shown that the matrix of the atomic Hamiltonian $H(r)$, Eq.(20), which contains $N_e$ bound electrons is always factorized, i.e. it is represented in the form

$$H = \Theta^*_1(r) \Theta_1(r) + \hat{a}_1$$

(21)

where $\hat{a}_1$ is a matrix defined below, while the operator $\Theta_1(r)$ and its adjoint operator $\Theta^*_1(r)$ are the first-order differential operators defined as follows

$$\Theta_1(r) = \frac{1}{\sqrt{2}} \left[ -\left( \frac{\partial}{\partial r} + \frac{3N_e - 1}{2r} \right) + \frac{\hat{\beta}_1}{r} + \hat{a}_1 \right]$$

(22)

and

$$\Theta^*_1(r) = \frac{1}{\sqrt{2}} \left[ \left( \frac{\partial}{\partial r} + \frac{3N_e - 1}{2r} \right) + \frac{\hat{\beta}_1}{r} + \hat{a}_1 \right]$$

(23)

where the notations $\hat{\beta}_1, \hat{\alpha}_1$ and $\hat{a}_1$ in Eqs.(21) - (23) stand for the symmetric, infinite-dimensional, in principle, matrices which do not commute with each other. In actual applications the dimensions of these matrices coincide with the total number of hyperspherical harmonics used. By substituting these two expressions, Eqs.(22) - (23), into Eq.(21) one finds the three following equations for the $\hat{\alpha}_1, \hat{\beta}_1$ and $\hat{a}_1$ matrices:

$$\hat{\beta}_1(\hat{\beta}_1 - 1) = \left( \hat{K} + \frac{3N_e - 1}{2} \right) \left( \hat{K} + \frac{3N_e - 1}{2} - 1 \right)$$

(24)

$$\hat{\alpha}_1 \hat{\beta}_1 + \hat{\beta}_1 \hat{\alpha}_1 = 2\hat{W}$$

(25)

$$\hat{a}_1 = -\frac{1}{2} \hat{\beta}_1^2$$

(26)
where the matrix of hypermomentum $\hat{K}$ is a diagonal matrix in the basis of hyperspherical harmonics (or, in $K-$representation, for short). Solution of Eq.(24) is written in the form
\[ \hat{\beta}_1 = \hat{K} + \frac{3N_e - 1}{2} \] (27)
where we use the fact that the atomic wave function is regular at $r = 0$, or at the atomic nucleus. As follows from this equation the matrix $\hat{\beta}_1$ is diagonal in $K-$representation. Below, we apply only this $K-$representation, since it substantially simplifies a large number of formulas derived below. In particular, by using Eq.(25) and the formula from [23] (see Chapter 10, § 18) we can write the explicit expression for the $\hat{\alpha}_1$ matrix
\[ \hat{\alpha}_1 = \frac{2}{\sqrt{2}} \int_0^{+\infty} \exp(-\hat{\beta}_1 t) \hat{W} \exp(-\hat{\beta}_1 t) dt \] (28)
Since the $\hat{\beta}_1$ matrix is diagonal, then for the $(ij)$-matrix element of the $\hat{\alpha}_1$ matrix takes the form
\[ [\hat{\alpha}_1]_{ij} = \frac{2W_{ij}}{[\hat{\beta}_1]_{ii} + [\hat{\beta}_1]_{jj}} = \frac{2W_{ij}}{K_i + K_j + 3N_e - 1} \] (29)
Finally, we can determine the $\hat{\alpha}_1$ matrix from Eq.(26). In particular, for the $(ij)$-matrix elements of the $\hat{\alpha}_1$ matrix one finds
\[ [\hat{\alpha}_1]_{ij} = -2 \sum_k \frac{W_{ik}}{\beta_i + \beta_k} \cdot \frac{W_{kj}}{\beta_k + \beta_j} = -2 \sum_k \frac{1}{\beta_i + \beta_k} [W_{ik}W_{kj}] \frac{1}{\beta_k + \beta_j} \] (30)
At the second stage of the procedure, we introduce the set of radial operators $\Theta_n(r)$, where $n = 2, 3, \ldots$, which are similar to the operator $\Theta_1(r)$ defined above (see, Eq.(22)), i.e.
\[ \Theta_n(r) = \frac{1}{\sqrt{2}} \left[ -\left( \frac{\partial}{\partial r} + \frac{3N_e - 1}{2r} \right) + \frac{\hat{\beta}_n}{r} + \hat{\alpha}_n \right] \] (31)
Therefore, its adjoint operator takes the form
\[ \Theta_n^*(r) = \frac{1}{\sqrt{2}} \left[ \left( \frac{\partial}{\partial r} + \frac{3N_e - 1}{2r} \right) + \frac{\hat{\beta}_n}{r} + \hat{\alpha}_n \right] \] (32)
In order to construct the correct and logically closed algorithm of the factorization method the following conditions must be obeyed
\[ \Theta_n(r)\Theta_n^*(r) + \hat{\alpha}_n = H_{n+1} = \Theta_{n+1}^*(r)\Theta_{n+1}(r) + \hat{\alpha}_{n+1} \] (33)
for $n = 1, 2, \ldots$. By substituting the explicit expressions, Eqs.(31) and (32) into Eq.(33) we obtain the following equations for the $\hat{\beta}_n, \hat{\beta}_{n+1}, \hat{\alpha}_n, \hat{\alpha}_{n+1}, \hat{\beta}_n$ and $\hat{\alpha}_{n+1}$ matrices
\[ \hat{\beta}_{n+1}(\hat{\beta}_{n+1} - 1) = \hat{\beta}_n(\hat{\beta}_n + 1) \] (34)
\[ \hat{\alpha}_n\hat{\beta}_n + \hat{\beta}_n\hat{\alpha}_n = 2\hat{W} = \alpha_{n+1}\hat{\beta}_{n+1} + \beta_{n+1}\hat{\alpha}_{n+1} \] (35)
\[ \hat{\alpha}_n = -\frac{1}{2}\alpha_n^2 \] (36)
These matrix equations look very similar to the analogous numerical equations mentioned in Section II (see, Eqs.(9)). However, these equations Eqs.(34) - (36), are written for the symmetric, infinite-dimensional matrices, which do not commute with each other, e.g., the \( \hat{\beta}_n \) matrix do not commute with the \( \hat{\alpha}_n \) and \( \hat{\alpha}_{n+1} \) matrices, etc. Solution of these equations, Eqs.(34) - (36), regular at \( r = 0 \) is written in the following form(s)

\[
\hat{\beta}_{n+1} = \hat{\beta}_n + 1 = \ldots = \hat{\beta}_1 + n = \hat{K} + \frac{3N_e - 1}{2} + n \tag{37}
\]

\[
\hat{\alpha}_{n+1} = 2 \int_0^{+\infty} \exp(-\hat{\beta}_{n+1}t) \hat{W} \exp(-\hat{\beta}_{n+1}t) dt \tag{38}
\]

\[
\hat{a}_{n+1} = -\frac{1}{2} \alpha_{n+1}^2 \tag{39}
\]

The second equation, Eq.(38), produces the following explicit expression for the \((ij)\)–matrix element of the \( \hat{\alpha}_{n+1} \) matrix

\[
\left[ \hat{\alpha}_{n+1} \right]_{ij} = \frac{2W_{ij}}{[\beta_{n+1}]_{ii} + [\beta_{n+1}]_{jj}} = \frac{2W_{ij}}{[\beta_1]_i + [\beta_1]_j + 2n} = \frac{2W_{ij}}{K_i + K_j + 3N_e - 1 + 2n} \tag{40}
\]

where \([\beta_{n+1}]_{ij}\) is the diagonal \((ii)\)–matrix element of the diagonal \( \hat{\beta}_1 \) matrix, i.e. \([\beta_{n+1}]_{ij} = \delta_{ij}[\beta_{n+1}]_{ii} = \delta_{ij}[\beta_1]_i\) and \([\beta_1]_{ij} = \delta_{ij}[\beta_1]_i = \delta_{ij}[\beta_1]_i\). This leads to the following analytical formula for the \((ij)\)–matrix elements of the \( \hat{\alpha}_{n+1} \) matrix

\[
\left[ \hat{\alpha}_{n+1} \right]_{ij} = -2 \sum_k \frac{W_{ik}}{[\beta_1]_i + [\beta_1]_k + 2n} \cdot \frac{W_{kj}}{[\beta_1]_k + [\beta_1]_j + 2n} \tag{41}
\]

\[
= -2 \sum_k \frac{1}{b_{ik} + n} \left[ W_{ik}W_{kj} \right] \frac{1}{b_{kj} + n} \frac{1}{K_i + K_k + 2n + 3N_e - 1} \left[ W_{ik}W_{kj} \right] \frac{1}{K_k + K_j + 2n + 3N_e - 1} \tag{41}
\]

where \( b_{ik} = \frac{1}{2}([\beta_1]_i + [\beta_1]_k) \) and \( b_{kj} = \frac{1}{2}([\beta_1]_k + [\beta_1]_j) \), while \( K_i \) are the matrix elements of the diagonal \( \hat{K} \)-matrix (the matrix of hypermomentum) and \( n \geq 0 \), where \( n \) is the radial quantum number (integer, non-negative). Formally, the formula, Eq.(41), is a direct generalization of the Bohr’s formula, originally derived by N. Bohr (in 1913) for the hydrogen atom, to an atom/ion which contains \( N_e \) bound electrons. In Quantum Mechanics the same formula for the spectra of the hydrogen atom was derived by W. Pauli in 1926 \[24\]. For \( N_e = 1 \) the formula Eq.(41) exactly coincides with the formula Eq.(3) (in atomic units). Indeed, in this case \( 3N_e - 1 = 2 \), \( \hat{W}_{ij} = -Q\delta_{ij}, K_i = K_j = \ell \) and \( \ell \) is the good quantum number. Therefore, one finds from Eq.(41) \( E_i = \left[ \hat{\alpha}_{n+1} \right]_{ii} = -\frac{Q^2}{2(\ell+1+n)^2} \). For few- and many-electron atoms the situation is more complicated, since for such systems we need to know
the explicit forms of the radial part of the total wave functions. This problem is discussed in the next Section.

V. BOUND STATE WAVE FUNCTIONS

Let us discuss an approach which can be used to determine the wave functions of the bound states in atoms/ions which contain $N_e$ ($N_e \geq 1$) bound electrons. This approach is based on the basic equations of matrix mechanics derived above and has a number of similarities with the analogous method used in Section II for one-electron atoms and ions. In particular, the ground (bound) state wave functions can be determined from the differential equation of the first order $\Theta_1(r)\Psi(r) = 0$. The explicit form of this equation is

$$[-\left(\frac{\partial}{\partial r} + \frac{3N_e - 1}{2r}\right) + \frac{\hat{\beta}_1}{r} + \hat{\alpha}_1] \Psi(r) = 0$$

where $\hat{K}$ is the diagonal matrix of the hypermomentum, i.e. $\hat{K} = \hat{\beta}_1 - \frac{3N_e + 1}{2}$. To solve this equation we can represent the function $\Psi(r)$ in the form $\Psi(r) = r^K \exp(\lambda r) C$, where $\lambda$ is a real (always negative) numerical constant defined below and $C$ is the numerical vector, i.e. each component of this vector does not depend upon the hyper-radius $r$. Substitution of the function $\Psi(r)$ in this form into Eq.(42) reduces this equation to the form

$$[-\hat{K} - \lambda + \hat{K} + \hat{\alpha}_1] \Psi(r) = [\hat{\alpha}_1 - \lambda] r^K \exp(\lambda r) C = 0$$

In other words, to determine the numerical value of $\lambda$ ($\lambda < 0$ or $\lambda = -|\lambda|$) we need to solve the following generalized eigenvalue problem: $(\hat{A} - \lambda\hat{B})C = 0$, where the matrix elements of the $\hat{A}$ and $\hat{B}$ matrices are defined by the following equations

$$[\hat{A}]_{ij} = \frac{1}{N_i N_j} \int_0^{+\infty} r^{K_i}(\hat{\alpha}_1)_{ij} r^{K_j} \exp(2\lambda r)r^{3N_e-1} dr = \frac{\Gamma(K_i + K_j + 3N_e)}{N_i N_j (2 | \lambda |)^{K_i + K_j + 3N_e}} (\hat{\alpha}_1)_{ij}$$

$$[\hat{B}]_{ij} = \frac{\delta_{ij}}{N_i^2} \int_0^{+\infty} r^{2K_i} \exp(2\lambda r)r^{3N_e-1} dr = \frac{\Gamma(2K_i + 3N_e)}{N_i^2 (2 | \lambda |)^{2K_i + 3N_e}}$$

where $\Gamma(x)$ is the Euler $\Gamma$–function. In actual applications the numbers $K_i, K_j$ and $N_e$ are integer and we can apply the formula $\Gamma(a) = (a - 1)!$ As follows from the second equations the matrix $\hat{B}$ is diagonal and all its eigenvalues (i.e. diagonal elements) are positive. Now, we can choose the normalization constant $N_i$ in Eq.(45) as follows

$$N_i = \sqrt{\frac{(2 | \lambda |)^{2K_i + 3N_e}}{\Gamma(2K_i + 3N_e)}}$$
This transforms the matrix $\hat{B}$ into the unit matrix. The original problem is reduced to the regular eigenvalue problem, i.e. to the equation $(\hat{A} - \lambda)C = 0$, where $\hat{A}$ is the $\hat{A}$ matrix in the new 'normalized' basis, i.e.

$$[\hat{A}]_{ij} = \frac{\Gamma(K_i + K_j + 3N_e)}{\sqrt{\Gamma(2K_i + 3N_e)\Gamma(2K_j + 3N_e)}}(\hat{\alpha}_1)_{ij}$$  \hspace{1cm} (47)$$

Note that the matrix elements of this matrix $(\hat{A})$ do not depend (explicitly) upon $\lambda$. If we know the numerical value of $\lambda$, then the total energy of the lowest energy state in the term is $E_1 = -\frac{1}{2}\lambda^2$.

The eigenvalue problem discussed above is equivalent to the finding of the absolute minimum of the following energy functional $E_1(\Psi)$

$$E_1(\Psi) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi | \Theta_1(r)\Theta_1(r) | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \frac{\langle \Psi | \hat{a}_1 | \Psi \rangle}{\langle \Psi | \Psi \rangle} \hspace{1cm} (48)$$

In our strategy of minimization the trial wave functions is represented in the form of the linear combinations: $\Psi(r) = r^{\hat{K}}\exp(\lambda r)C = \sum_{n=1}^{N} C_n r^{\hat{K}_n}\exp(\lambda r) = C_n r^{\hat{K}_n}\exp(\lambda r)$. The first term in the right-hand side of Eq.(48) is always non-negative. For our choice of the radial trial functions this term equals zero identically. The second term in the right-hand side of Eq.(48) is always negative. Optimization of the linear coefficients $C_k$ in our wave function at the second stage of the method means that we are trying to make the second term in Eq.(48) as negative as possible.

The wave functions of the excited state in the atoms/ions with the $N_e$ bound electrons are determined analogously. Let us briefly describe this process by omitting some obvious details. The equation which determines the wave function of the $n$–th excited states $(\Psi_n(r))$ takes the form

$$\Theta_n(r)\Psi_n(r) = \left[ -\frac{\partial}{\partial r} + \frac{\hat{K} + n}{r} + \hat{\alpha}_1 \right] \Psi_n(r) = 0$$  \hspace{1cm} (49)$$

To solve this equation we represent the wave function $\Psi_n(r)$ in the form $\Psi_n(r) = r^{\hat{K}+n}\exp(\lambda_n r)C_n$, where $\lambda_n$ is a real (and negative) numerical constant defined below and $C_n$ is the $r$–independent constant vector. By substituting

$$\left[ -\frac{\hat{K} + n}{r} - \lambda_n + \frac{\hat{K} + n}{r} + \hat{\alpha}_n \right] \Psi_n(r) = \left[ \hat{\alpha}_n - \lambda_n \right] r^{\hat{K}+n}\exp(\lambda_n r)C_n = 0$$  \hspace{1cm} (50)$$

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This problem is reduced to the solution of the following generalized eigenvalue problem: 
\((\hat{A}_n - \lambda \hat{B}_n)C_n = 0\), where the matrix elements of the \(\hat{A}_n\) and \(\hat{B}_n\) matrices are defined by the following equations

\[
[\hat{A}_n]_{ij} = \frac{1}{N_i N_j} \int_0^{+\infty} r^{K_i+n} (\hat{\alpha}_n)_{ij} r^{K_j+n} \exp(2\lambda_n r)r^{3N_e-1}dr 
\]

\[
[\hat{B}_n]_{ij} = \frac{\delta_{ij}}{N^2} \int_0^{+\infty} r^{2K_i+2n} \exp(2\lambda_n r)r^{3N_e-1}dr 
\]

where the matrix \(\hat{B}_n\) is diagonal and all its eigenvalues (i.e. diagonal elements) are positive. Again, we can choose the normalization constants \(N_i\) in the form

\[
N_i = \sqrt{\frac{(2 \mid \lambda \mid)^{2K_i+2n+3N_e}}{\Gamma(2K_i+2n+3N_e)}} 
\]

In this case the matrix \(\hat{B}_n\) will coincide with the unit matrix. This reduces the original problem to the regular eigenvalue problem, i.e. \((\hat{A}(n) - \lambda_n)C_n = 0\), where \(\lambda_n\) is the lowest eigenvalue of the \(\hat{A}(n)\) matrix which is the matrix \(\hat{A}_n\) in the new ‘normalized’ basis, i.e.

\[
[\hat{A}(n)]_{ij} = \frac{\Gamma(K_i + K_j + 2n + 3N_e)}{\sqrt{\Gamma(2K_i+2n+3N_e)\Gamma(2K_j+2n+3N_e)}} (\hat{\alpha}_n)_{ij} 
\]

where \(n \geq 1\). Again, we note that the matrix elements of this matrix \((\hat{A}(n))\) do not depend (explicitly) upon \(\lambda\). The known numerical value of \(\lambda_n\) determines the total energy of the \(n\)-th excited bound state in the same atomic term term: \(E_{n+1} = -\frac{1}{2}\lambda^2_n\). Thus, by using the method of matrix factorization developed in this study one can find all bound states in one atomic term and their wave functions. Such wave functions must be orthogonalized to each other to form a set of actual wave functions. Note also that the matrices \(\hat{\alpha}_n\) and \(\hat{\alpha}_{n+1}\) which are used in this method are closely related to each other. Indeed, the \(\hat{\alpha}_{n+1}\) matrix easily obtained from the ‘previous’ \(\hat{\alpha}_n\) matrix by adding the term +1 in its denominator. i.e. by the replacement \(n \rightarrow n + 1\).

Furthermore, as follows from Eq. (54) for any given bound state in many-electron atoms the radial quantum number \(n\) is a conserving quantum number which can be used to number (or locate) this bound state inside of one series of bound states which have the same values of \(L, L_z(\text{or} M), S, S_z\) and \(\pi\). In other words, this radial quantum number \(n\) (or excitation index) can be used to number the bound states inside of one atomic term. In general, any bound state in the atomic term can be designated by the notation \(|n, [L, M, S, S_z, \pi]\|\).
where the internal notation \([L, M, S, S_z, \pi]\) designates the corresponding atomic term and \(n\) is the number of this (bound) state in this atomic term, or, in other words, the number of excitation(s). The same notation \(|n, [L, M, S, S_z, \pi]|\) can be used to designate the corresponding wave function(s). This ‘conservation’ of the ‘radial’ quantum number \(n\) (in our current notation) allows one to designate the bound states in few- and many-electron atoms. For instance, the ground bound (doublet) state in the lithium atom can be designated by the notation \(1^2S\)-state (instead of the \(2^2S\) notation used currently).

VI. APPLICATIONS AND CONCLUSIONS

We have developed the method of matrix factorization which can be applied to many-electron (or many-particle) atoms, ions and molecules. Formally, this method can be used for arbitrary many-body systems where each pair of particles interacts by the Coulomb potential. Briefly, for each of these systems the corresponding Hamiltonian written in the hyperspherical multi-dimensional coordinates must be similar to the form of Eq.(18) ([11]-[13]). The main difference between the matrix factorization and ‘regular’ (or numerical) factorization follows from the fact that in the method of matrix factorization we use a number of infinite-dimensional matrices which do not commute with each other. This fact complicates the procedure of matrix factorization and its applications to many-electron atomic systems. Nevertheless, we could develop the logically closed algorithm of the matrix factorization, and now this method can be applied to determine the bound states in a large number of actual (i.e. few- and many-electron) atomic systems.

At the first step of the procedure we need to calculate the (symmetric) matrix of the potential energy \(\hat{W}\) in the basis of the physical hyperspherical harmonics constructed for some atomic term \([L, M, S, S_z, \pi]\). By using this matrix it is easy to construct an infinite, in principle, consequence of matrices \(\hat{A}(n)\) each of which has the following matrix elements

\[
[\hat{A}(n)]_{ij} = \frac{\Gamma(K_i + K_j + 2n + 3N_e)}{\sqrt{\Gamma(2K_i + 2n + 3N_e)\Gamma(2K_j + 2n + 3N_e)}} \cdot \frac{2W_{ij}}{K_i + K_j + 3N_e - 2n}\]

\[
= \frac{(K_i + K_j + 2n + 3N_e - 1)!}{\sqrt{(2K_i + 2n + 3N_e - 1)!(2K_j + 2n + 3N_e - 1)!}} \cdot \frac{2W_{ij}}{K_i + K_j + 3N_e - 1 + 2n}
\]

where \(n = 0, 1, 2, \ldots\). The matrix \([\hat{A}(n)]\) is symmetric and all its eigenvalues are negative. At the second stage of the procedure we determine the lowest eigenvalue \(\lambda_{n+1}\) of each of
these matrices $\hat{A}(n)$, where $n = 0, 1, 2, \ldots$. The total energies $E_{n+1}$ of the corresponding bound states in the atom/ion with $N_e$ bound electrons are simply related with the $\lambda_{n+1}$ eigenvalues by the formula $E_{n+1} = -\frac{1}{2}\lambda_{n+1}^2$. This gives us the complete energy spectrum of bound state for this atomic term $[L, M, S, S_z, \pi]$. To find the corresponding wave functions one needs to use the procedure described in the previous Section which must include the orthogonalization of the set of wave functions with different $n$ at the final step. Briefly, to obtain the total energies of all bound states in one atomic term in our method we need to determine the lowest eigenvalue for each of the matrices which are included in the following (infinite) consequence of closely related matrices $\hat{A}(1), \hat{A}(2), \ldots, \hat{A}(n), \hat{A}(n+1), \ldots$. The matrix $\hat{A}(n+1)$ is obtained from the matrix $\hat{A}(n)$ by replacing the radial quantum number $n$ in Eq.(55) by the ‘next’ $n+1$ value.

For one-electron atomic systems when $N_e = 1$ we have in Eq.(55) $K_i = K_j = \ell, W_{ij} = -Q\delta_{ij}$ and $\ell$ is the conserving quantum number of atomic angular moment. This leads to the answer known for the hydrogen-like atom/ions discussed above. An additional interesting fact follows directly from Eq.(55) where each term in the right-hand side depends upon the $n+\ell$ sum only (not, e.g., upon the $n+2\ell$ and/or $n+\frac{1}{2}\ell$ sums). This fact is closely related to an additional symmetry of the bound states in one-electron atom/ions, since we can replace the conserving quantum number $n$ (or $n_r$ in usual notation) by the $\ell$ quantum number and vice versa. The total energy will not change during such substitutions. For atoms with $N_e \geq 2$ such a replacement has no sense, since the hyper-radial quantum number $n$ (or $n_r$) is a conserving quantum number, while an arbitrary component of the diagonal matrix of hypermomentum ($K_i$ and $K_j$) does not conserve.

The method of matrix factorization developed in this study has been applied to the variational bound state calculations of bound states in the $^1S$ atomic term of the helium atom. In our calculations we have used 576 hyperspherical harmonics (HH). In particular, we have used all hyperspherical harmonics from the families of HH up to $K_{\max} = 40$, some selected HH from families from $K_{\max} = 44$ up to $K_{\max} = 52$ and only main HH from the families of HH from $K_{\max} = 56$ up to $K_{\max} = 100$. The physical sense of the main hyperspherical harmonics was explained in detail in [17]. The main hyperspherical harmonics for the bound states in the $^1S$–term of the He atom have the from $|K, \ell \rangle = |4k, 0\rangle$, where $k$ is any non-negative integer number. The total energies of some lower-lying bound states in the $^1S$–term in the He atom obtained by using our method of matrix factorization are
$E_1 = -2.9037175 \text{ a.u.}, \ E_2 = -2.144954 \text{ a.u.}, \ E_3 = -2.06033 \text{ a.u.}, \ E_4 = -2.0318 \text{ a.u.}$

The ‘exact’ total energies obtained in our earlier calculations for these bound states are $E_1 = -2.903724377034115924519405(5) \text{ a.u.}, \ E_2 = -2.145974046054417415(10) \text{ a.u.}, \ E_3 = -2.06127198974090848(5) \text{ a.u.}, \ E_4 = -2.03358671703072520(7) \text{ a.u.}$

These values are significantly more accurate than the total energies found with the use of our procedure based on the hyperspherical harmonics. This can be explained by the known fact (see, e.g., [14]) that hyperspherical expansion is not very effective approach to describe electron-electron correlations in actual atoms and ions. However, the overall accuracy of the method based on the hyperspherical expansion can be increased drastically, e.g., by increasing the total number of the main HH used and/or by considering the coherent hyperspherical states.

The method of matrix factorization allows one to determine the bound state spectra of many-electron (but non-relativistic!) atoms, ions and molecules. This means that by using our method one can determine, in principle, all bound state energies and corresponding wave functions. At the following stages these wave functions can be applied to evaluate various bound state properties, including lowest-order relativistic and QED corrections for different atoms, ions and molecules. Formally, the method of matrix factorization allows one to obtain analytical and semi-analytical answers to numerous questions about atomic structure of the few- and many-electron (non-relativistic) atoms, ions and light molecules. In many cases, however, the obtained answers and solutions are often written in the matrix form which is directly related to the original matrix form of the matrix (quantum) mechanics.

It should be mentioned that since Niels Bohr published (in 1912) his famous formula for the energy levels in the hydrogen atom a large number of people have tried to derive analogous formulas for few- and many-particle atoms and ions. In some studies it was assumed that all bound state of an atom can be found as the roots of some polynomial/analytical function, while another direction was based on analytical/numerical diagonalization of some ‘universal’ matrix. All these attempts have failed. Equations derived in this study explain the reasons of such a failure. Note also that our method of matrix factorization of the Coulomb many-particle Hamiltonians has been developed with a substantial time delay. The basic equations of the method of matrix factorization have been produced at the end of 1978 when I was a student. Nevertheless, the complete version of the method has been formulated only in April this year. Unfortunately, this paper cannot be published in the middle of 1950’s, or even earlier, when Dirac, Fock and Heisenberg were around. At the same time
a large number of competing computational methods have extensively been developed and applied to atomic physics. Some of these methods became very effective, relatively simple and fast procedures. However, even now the method of matrix factorization has a great potential for future development and various modifications, since it is based on the internal ‘ladder’ structure of the Coulomb Hamiltonians. Furthermore, the matrix factorization is the new, relatively simple and advanced approach which can be used to investigate the few- and many-body Coulomb problems and determine the bound states in such systems. In particular, our method can be used to understand some interesting details of atomic spectra and substantially simplify accurate bound state computations of different systems known in atomic and molecular physics.

Finally, we want to emphasize that the method of matrix factorization is substantially based on the ladder structure of the Hamiltonians of the Coulomb many-body systems. In this study we discovered the method which uses this ladder structure of the Coulomb Hamiltonians and allows one to determine all bound states in any few- and/or many-body Coulomb system. Based on the ladder structure of the Coulomb Hamiltonians we can predict that this method can be used as a very effective tool for theoretical and numerical investigation of the bound state spectra in all Coulomb atomic and molecular systems. For instance, the method of matrix factorization allows one to study general dependencies of the total energies of different bound states in the few- and many-electron atoms/ions upon good quantum numbers \textit{a priori} known for such quantum systems. Note also that for Coulomb three-body systems we have developed another method \cite{26} which is also based on the ladder structure of the Hamiltonians, but allows one to obtain the corresponding eigenvalues (and eigenfunctions) to substantially better accuracy.

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