Nonrelativistic energy levels of helium atoms

D. T. Aznabaev,[1,2,3] A. K. Bekbaev,[1,4] and Vladimir I. Korobov[1,5]

[1]*Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia*
[2]*The Institute of Nuclear Physics, Ministry of Energy of the Republic of Kazakhstan, 050032 Almaty, Kazakhstan*
[3]*L.N. Gumilyov Eurasian National University, 010000 Astana, Kazakhstan*
[4]*Al-Farabi Kazakh National University, 050038 Almaty, Kazakhstan*
[5]*Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow 117198, Russia*

The nonrelativistic ionization energy levels of a helium atom are calculated for S, P, D, and F states. The calculations are based on the variational method of "exponential" expansion. The convergence of the calculated energy levels is studied as a function of the number of basis functions N. This allows us to claim that the obtained energy values (including the values for the states with a nonzero angular momentum) are accurate up to 28–35 significant digits. Calculations of the nonrelativistic ionization energy of the negative hydrogen ion H^- are also presented.

I. INTRODUCTION

The quantum problem of three bodies with Coulomb interaction is one of the most notable nonintegrable problems in quantum mechanics. At the same time, extremely accurate numerical solutions for the problem of bound states for a system of three particles may be obtained with modern computers. For example, the nonrelativistic energy of the ground state of helium with a nucleus of an infinite mass is now known accurately to 46 significant digits [1].

In the present study, a version of the variational method (the so-called "exponential" expansion) that allows one to numerically solve the quantum Coulomb three-body bound-state problem with a very high precision, which is easily applicable as well to the states with a nonzero angular momentum, is considered. This method is used to calculate the nonrelativistic ionization energies of a helium atom for S, P, D, and F states. It is shown that the developed method is an efficient and flexible instrument for studying Coulomb systems. An analysis of convergence proves that the method is highly accurate and demonstrates that nonrelativistic energies accurate up to 28–35 significant digits may be obtained with rather moderate efforts.

Developing such high-precision methods is of importance for the reason that it may help in solving a wide variety of problems that are of interest in physics. For example, antiprotonic helium atoms are of particular interest, which allows for high-precision studies of the energy spectrum of this exotic system and inferring various properties of an antiproton from comparison of theory and experiment [2,3]. Here it is worth mentioning recent interest in antiprotonic helium as a tool for constraints on various fifth forces [4,5] to set general limits on new interactions beyond the standard model.

Another important aspect, namely, the cross impact of atomic and nuclear physics [6], in the determination of statistical parameters of nuclei should be noted. For example, the accuracy of the mean-square helium charge radius that is determined experimentally from electron-nuclei scattering is about 1%–3%. At the same time, the experimental determination of the charge radius of ^{4}He by muonic atom spectroscopy [7] allows one to reduce the error in the value of this parameter by more than an order of magnitude.

One more application is the numerical-analytical studies of the critical nuclear charge Z_c for two-electron atoms [8] and the $1/Z$ expansion of the binding energy [9], where the high-precision calculations are extremely crucial.

The paper is structured as follows. The variational principle and application of the variational Ritz method to the stationary Schrödinger problem is discussed in detail in Secs. I and II. In particular, the variational "exponential" expansion used in practical calculations is formulated. The inverse iteration method, which is considered to be one of the most efficient computational tools to solve an eigenvalue problem for a finite basis, is presented in Sec. III. In the last section, the numerical calculations are reviewed and the final theoretical results for 19 states of a helium atom as well as the most accurate so far estimate for the ground-state energy of H^- ions are given.

II. VARIATIONAL METHOD

Let us first formulate the variational principle for bound states.

The Hylleraas-Undheim variational principle, which is better known in mathematics as the Rayleigh-Ritz variational principle, is the starting point in solving the stationary Schrödinger equation,

$$H\psi = E\psi, \tag{1}$$

for a certain Hamiltonian using variational methods. This principle is considered a versatile method for deriving an approximate solution. The problems of determining the extrema or stationary values of functionals are the basic problems of variational calculation. The essence of this method consists of substituting the problem of finding the stationary values of functionals with a fundamentally less complex problem of

finding the stationary values of functions of several variables [10].

Let there be a self-adjoint operator defined within the Hilbert space for which the following boundedness condition is satisfied:

$$H \geqslant cI, \qquad (2)$$

where c is a certain constant. Let us then define a functional

$$\Phi(\psi) = \frac{(\psi, H\psi)}{(\psi, \psi)} \qquad (3)$$

that is bounded from below by c. The following theorem is valid:

Theorem [10]. Let H be a self-adjoint operator that satisfies condition (2). Let us define

$$\mu_n(H) = \max_{\dim \chi = n-1} \min_{\substack{\Psi \in \mathcal{D}(H) \\ \Psi \in \chi^\perp}} \Phi(\Psi), \qquad (4)$$

where $\chi^\perp$ is a subspace orthogonal to χ, and $D(H)$ is the domain of operator H. One of the following assertions is then true for any fixed n:

(a) n eigenvalues (degenerate eigenvalues are counted according to their multiplicity) lying below the essential spectrum boundary are present and $\mu_n(H)$ is the nth eigenvalue (with account of multiplicity); or

(b) $\mu_n(H)$ is the lower boundary of the essential spectrum.

The determination of eigenvalues (i.e., the energy of bound states of the stationary Schrödinger equation) comes down to calculating the saddle points of functional (4). The assertion of the theorem is known as the minimax principle.

Let us now consider a method that uses the Rayleigh-Ritz variational principle to solve practical eigenvalue problems called the Ritz process. Let ϕ_k be a complete sequence of vectors in the Hilbert space subject to the following conditions:

(1) Vectors ϕ_k belong to the domain of operator H;

(2) Vectors $\phi_1, \phi_2, \dots, \phi_n$ are linearly independent at any n.

Let us assume that $u_n = \sum_{k=1}^n x_k \phi_k$, where x_k are scalar coefficients. Inserting u_n [at fixed n into functional $\Phi(\cdot)$] one obtains a function that depends on a finite set of parameters $\{x_n\}_1^n$,

$$\Phi(x) = \left(\sum_{i,j=1}^n a_{ij} x_i x_j \right) \Big/ \left(\sum_{i,j=1}^n b_{ij} x_i x_j \right), \qquad (5)$$

where

$$a_{ij} = (\phi_i, H\phi_j), \quad b_{ij} = (\phi_i, \phi_j). \qquad (6)$$

The determination of minimax solutions is thus reduced to calculating the corresponding eigenvalues of the generalized eigenvalue problem:

$$Ax = \lambda Bx, \qquad (7)$$

where matrices A and B are composed of coefficients a_{ij} and b_{ij}, respectively.

Vectors ϕ_k may depend on nonlinear parameters ω. If this is the case, problem (7) is solved for each fixed ω and each eigenvalue number k, $\lambda_k(\omega)$ is chosen, and this value is then minimized over all values of nonlinear parameters:

$$\lambda_k = \inf_\omega \lambda_k(\omega). \qquad (8)$$

One important condition is satisfied for Ritz estimates:

$$\mu_k(H) \leqslant \lambda_k. \qquad (9)$$

It follows from there that Ritz estimates are upper bounds. Inequality (9) for basis functions dependent on nonlinear parameters follows from

$$\mu_k(H) \leqslant \inf_\omega \lambda_k(\omega) = \lambda_k. \qquad (10)$$

A rigorous proof of the applicability of theorem 1 to the problems of nonrelativistic quantum mechanics with a Hamiltonian of the form

$$H = -\sum_{i=1}^n \frac{\Delta_i}{2m_i} + V(\mathbf{r}_1, \dots, \mathbf{r}_n), \qquad (11)$$

and a potential of a sufficiently general form that includes, among others, the Coulomb potential of interparticle interaction, was derived by Kato [11].

III. GENERALIZED HYLLERAAS EXPANSION

Let us consider the generalized Hylleraas expansion for the states of arbitrary total orbital momentum L [12]:

$$\psi(r_1, r_2)$$
$$= \sum_{l_1+l_2=\mathcal{L}} \mathcal{Y}_{LM}^{l_1 l_2}(r_1, r_2) \left[e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \sum_{l,m,n \geqslant 0} C_{lmn} r_1^l r_2^m r_{12}^n \right], \qquad (12)$$

where $\mathcal{L} = L$ for the states of "normal" spatial parity $\Pi = (-1)^L$, and $\mathcal{L} = L + 1$ for the states of "anomalous" spatial parity $\Pi = (-1)^{L+1}$. The $\mathcal{Y}_{LM}^{l_1 l_2}$ functions are regular bipolar spherical harmonics [13] that depend on two angular coordinates:

$$\mathcal{Y}_{LM}^{l_1 l_2}(r_1 r_2) = r_1^{l_1} r_2^{l_2} \{ Y_{l_1}(\hat{r}_1) \otimes Y_{l_2}(\hat{r}_2) \}_{LM},$$

and the spatial parity operator $P\psi = \pi\psi$ acts on the spatial coordinates in the following way: $P(r_1, r_2) \to (-r_1, -r_2)$. The ease of use of the $\mathcal{Y}_{LM}^{l_1 l_2}$ functions stems from the fact that they correctly reproduce the behavior of the wave function at $r_1 \to 0$ (or $r_2 \to 0$), and retain the reasonable requirement of boundedness of the function within the domain of variables for the expression within square brackets in Eq. (12).

The "normal" and "anomalous" spatial parities were designated this way for the following reason. It can be seen from expansion (12) that "anomalous" parity states in a dissociation limit may be decomposed into clusters with a bound pair, which may have only nonzero angular momentum, $l \geqslant 1$. In atomic physics, the ground state of a pair of particles has zero angular momentum, while the boundary of the continuum in a system of three particles is defined by the energy of the pair with the lowest ground energy, or zero (if no bound pairs are presented). It follows that bound "anomalous" parity states are normally located in the continuum of the three-particle system [14]. Therefore, these states are imbedded into the continuum and any perturbation violating spatial parity of the system makes them "true" resonances.

The calculation of matrix elements reduces to evaluating integrals of the following form:

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = \iint r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} dr_1 dr_2 dr_{12}.$$

(13)

Differentiating with respect to α under the integral sign, we obtain the following:

$$\left(-\frac{\partial}{\partial \alpha}\right)\Gamma_{l-1,mn}(\alpha, \beta, \gamma) = \Gamma_{lmn}(\alpha, \beta, \gamma).$$

Thus, all integrals may be evaluated from Γ_{000} by simple differentiation:

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = \left(-\frac{\partial}{\partial \alpha}\right)^l \left(-\frac{\partial}{\partial \beta}\right)^m \left(-\frac{\partial}{\partial \gamma}\right)^n \Gamma_{000}(\alpha, \beta, \gamma)$$

$$= \left(-\frac{\partial}{\partial \alpha}\right)^l \left(-\frac{\partial}{\partial \beta}\right)^m \left(-\frac{\partial}{\partial \gamma}\right)^n \left[\frac{2}{(\alpha + \beta)(\beta + \gamma)(\gamma + \alpha)}\right].$$

(14)

Following [15], we then use recurrence relation

$$\Gamma_{lm}(\alpha, \beta) = \frac{1}{\alpha + \beta}\left[\left(l\Gamma_{l-1,m} + m\Gamma_{l,m-1}\right) + \left(-\frac{\partial}{\partial \alpha}\right)^l \left(-\frac{\partial}{\partial \beta}\right)^m f(\alpha, \beta)\right].$$

Applying it successively to each pair of variables α, β, and γ, we arrive at the recurrence scheme for integral evaluation for non-negative values of parameters (l, m, n):

$$\Gamma_{lmn} = \frac{1}{\alpha + \beta}[l\Gamma_{l-1,m,n} + m\Gamma_{l,m-1,n} + B_{lmn}],$$

$$B_{lmn} = \frac{1}{\alpha + \beta}[lB_{l-1,m,n} + mB_{l,m-1,n} + A_{lmn}], \quad (15)$$

$$A_{lmn} = \delta_{l0}\frac{2(m+n)!}{(\beta + \gamma)^{m+n+1}}.$$

The fact that quantities A_{lmn}, B_{lmn}, and Γ_{lmn} in (15) are positive is an important feature of these relations that makes recurrence scheme (15) stable with respect to the round-off errors in computations. Averaging over angular variables for the states with a nonzero total orbital moment of the system was analyzed by Drake [12]. This averaging reduces the calculation of matrix elements for nonzero L to integrals of the type (13). A compact and efficient recurrence scheme that implements this reduction was proposed later by Efros [16]. The efficiency of the above-described variational expansions is the highest when they are applied to systems composed of two electrons and a heavy nucleus.

Let us now study "exponential" expansion in more detail. This expansion assumes the following form for S states:

$$\psi(r_1, r_2, r_{12}) = \sum_n C_n e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}}, \quad (16)$$

where the parameters in the exponent are chosen in one way or another. In early studies [17] that used expansion (16), the obtained representation was associated with the discretization of the integral representation of the wave function,

$$\psi(x_1, \ldots, x_A) = \int \varphi(x_1, \ldots, x_A; \alpha) f(\alpha) d\alpha, \quad (17)$$

that was proposed by Griffin and Wheeler [18] in 1957. The α_n, β_n, and γ_n parameters were chosen in accordance with

various quadrature integration formulas (17). The systematic study of expansion (16) with parameters generated using pseudorandom numbers was carried out in [19]. In the proposed approach, nonlinear parameters from Eq. (16) are generated using the following simple formulas:

$$\alpha_n = \left[\left\lfloor \tfrac{1}{2}n(n+1)\sqrt{p_\alpha} \right\rfloor (A_2 - A_1) + A_1\right],$$

$$\beta_n = \left[\left\lfloor \tfrac{1}{2}n(n+1)\sqrt{p_\beta} \right\rfloor (B_2 - B_1) + B_1\right], \quad (18)$$

$$\gamma_n = \left[\left\lfloor \tfrac{1}{2}n(n+1)\sqrt{p_\gamma} \right\rfloor (C_2 - C_1) + C_1\right],$$

where $\lfloor x \rfloor$ is the fractional part of x, and p_α, p_β, and p_γ are certain prime numbers. These simple generators of pseudorandom numbers have their advantage in the reproducibility of the results of variational calculations. The convergence rate of the exponential expansion with a pseudorandom strategy for choosing nonlinear parameters (18) is exceptionally high at the sets of basis functions of moderate dimensionalities (up to 100–200 test functions). Rapid basis degeneration that results in the loss of computational stability in the double-precision arithmetic by basis dimensionality $N = 200$ is among the disadvantages of the method.

Let us write out for convenience the exponential variational expansion in its complete form, which accounts for the angular dependence of the wave function that describes the rotational degrees of freedom:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l_1 + l_2 = \mathcal{L}} \mathcal{Y}_{LM}^{l_1 l_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) G_{l_1 l_2}^{L\pi}(r_1, r_2, r_{12}),$$

$$G_{l_1 l_2}^{L\pi}(r_1, r_2, r_{12}) = \sum_n C_n e^{-\alpha_n r_1 - \beta_n r_2 - \gamma_n r_{12}}, \quad (19)$$

where $\mathcal{L} = L$ or $L+1$ (depending on the spatial parity of the state) and the complex parameters in the exponent are generated in a pseudorandom way (18).

When the number of basis function N increases, one may observe that the convergence rate is slowing down. This may be attributed to the fact that the "exact" wave function of the

TABLE I. Convergence of the nonrelativistic energy of the ground state of a helium atom.

Basis (N)	E_{nr}
10000	−2.90372 43770 34119 59831 11592 45193 9
14000	−2.90372 43770 34119 59831 11592 45194 398
18000	−2.90372 43770 34119 59831 11592 45194 40432
22000	−2.90372 43770 34119 59831 11592 45194 40443

bound state for atomic helium has a logarithmic singularity at $r_1, r_2 \to 0$: $\rho^2 \ln \rho$, where $\rho = \sqrt{r_1^2 + r_2^2}$ is the hyperradius of two electrons [20]. In order to improve the situation, one should construct a multilayer variational expansion composed of several independent sets of basis functions, the optimal variational nonlinear parameters for which are found inde-

pendently. Thus, each set of basis functions defines the best approximation in a certain region of coordinates of the system. In the case of a helium atom, the regions should be enclosed within each other and be more and more compact in terms of the hyperradius ($\rho < \rho_n = a^n$, where $a \approx 0.1$ and $n = 1, 2, 3 \dots$). This strategy makes the exponential expansion an efficient and versatile computational method for bound states in the quantum three-body problem with Coulomb interaction. The capabilities of this method were demonstrated in [21,22].

IV. INVERSE ITERATION METHOD

It was shown in Sec. I that the stationary Schrödinger equation is reduced to the generalized symmetrical eigenvalue problem with the help of the Ritz procedure:

$$Ax = \lambda Bx, \tag{20}$$

TABLE II. Nonrelativistic energies of the S, P, D, and F states of a helium atom. N is the number of basis functions. The two lines represent two consecutive calculations with the largest basis sets to show convergent digits. The third line presents calculations by Drake and Yan [23].

State	N	E_{nr}	State	N	E_{nr}
1^1S	18000	−2.90372 43770 34119 59831 11592 45194 40432	4^1S	14000	−2.03358 67170 30725 44743 92926 44363 64
1^1S	22000	−2.90372 43770 34119 59831 11592 45194 40443	4^1S	18000	−2.03358 67170 30725 44743 92926 44363 87
2^1S	18000	−2.14597 40460 54417 41580 50289 75461 918	4^3S	14000	−2.03651 20830 98236 29958 03780 71617 853
2^1S	22000	−2.14597 40460 54417 41580 50289 75461 921	4^3S	16000	−2.03651 20830 98236 29958 03780 71617 874
	[23]	−2.14597 40460 5443(5)			
2^3S	14000	−2.17522 93782 36791 30573 89782 78206 81124	4^1P	18000	−2.03106 96504 50240 71475 89314 36090 3
2^3S	16000	−2.17522 93782 36791 30573 89782 78206 81125	4^1P	22000	−2.03106 96504 50240 71475 89314 36094 1
	[23]	−2.17522 93782 367912(1)		[23]	−2.03106 96504 5024(3)
2^1P	18000	−2.12384 30864 98101 35924 73331 42354	4^3P	18000	−2.03232 43542 96630 33195 38824 67087
2^1P	22000	−2.12384 30864 98101 35924 73331 42374	4^3P	22000	−2.03232 43542 96630 33195 38824 67103
	[23]	−2.12384 30864 98092(8)		[23]	−2.03232 43542 9662(2)
2^3P	16000	−2.13316 41907 79283 20514 69927 63793	4^1D	22000	−2.03127 98461 78684 99621 39438 073
2^3P	18000	−2.13316 41907 79283 20514 69927 63806	4^1D	26000	−2.03127 98461 78684 99621 39438 143
	[23]	−2.13316 41907 7927(1)		[23]	−2.03127 98461 78687(7)
3^1S	18000	−2.06127 19897 40908 65074 03499 37089 2816	4^3D	18000	−2.03128 88475 01795 53802 34920 591
3^1S	22000	−2.06127 19897 40908 65074 03499 37089 2824	4^3D	22000	−2.03128 88475 01795 53802 34920 630
				[23]	−2.03128 88475 01795(3)
3^3S	14000	−2.06868 90674 72457 19199 65329 11291 75048	4^1F	18000	−2.03125 51443 81748 60863 20824 071
3^3S	16000	−2.06868 90674 72457 19199 65329 11291 75049	4^1F	22000	−2.03125 51443 81748 60863 20824 079
				[23]	−2.03125 51443 81749(1)
3^1P	18000	−2.05514 63620 91943 53692 83410 913	4^3F	18000	−2.03125 51684 03245 39350 49887 2817
3^1P	22000	−2.05514 63620 91943 53692 83410 921	4^3F	22000	−2.03125 51684 03245 39350 49887 2846
	[23]	−2.05514 63620 9195(3)		[23]	−2.03125 51684 032454(6)
3^3P	18000	−2.05808 10842 74275 33134 26965 47197			
3^3P	22000	−2.05808 10842 74275 33134 26965 47203			
	[23]	−2.05808 10842 7428(4)			
3^1D	18000	−2.05562 07328 52246 48939 00994 819			
3^1D	22000	−2.05562 07328 52246 48939 00994 825			
	[23]	−2.05562 07328 52245(6)			
3^3D	18000	−2.05563 63094 53261 32711 49601 65840			
3^3D	22000	−2.05563 63094 53261 32711 49601 65851			
	[23]	−2.05563 63094 53261(4)			

TABLE III. Comparison of nonrelativistic energies of the ground state of a helium atom.

Author (year)	Ref.	N	Energy (in a.u.)
Drake *et al.* (2002)	[24]	2358	−2.90372 43770 34119 598311
Korobov (2002)	[22]	5200	−2.90372 43770 34119 59831 1159
Schwartz (2006)	[1]	24099	−2.90372 43770 34119 59831 11592 45194 40444 66969 25310
Nakashima, Nakatsuji (2007)	[26]	22709	−2.90372 43770 34119 59831 11592 45194 40444 66969
This work		22000	−2.90372 43770 34119 59831 11592 45194 40443

where A is a symmetric matrix and B is a symmetric positive-definite matrix. The standard diagonalization procedure may be used to solve Eq. (20). In order to do that, the matrix $B = LL^T$ is expanded into a product of upper and lower triangular matrices and the problem is reduced to the standard symmetrical eigenvalue problem

$$A^{'} y = \lambda y, \tag{21}$$

where

$$A^{'} = L^{-1} A L^{-T}, \quad y = L^T x. \tag{22}$$

However, this method is too laborious ($\sim 20 N^3$ multiplication operations) and is less resistant to calculation errors. If only a single eigenvalue (eigenvector) is needed, the solution may be obtained efficiently ($\sim N^3/6$ multiplication operations) with the help of the inverse iteration method,

$$(A - \mu) x_k^{(n+1)} = s^{(n)} x_k^{(n)}, \tag{23}$$

where the scalar factor $s^{(n)}$ is chosen in such a way that $\|x_k^{(n+1)}\| = 1$. If μ is close to the exact eigenvalue λ_k, the vector sequence $x_k^{(n)}$ converges rapidly to the exact eigenvector x_k, and $\lambda_k^{(n)} = (x_k^{(n)}, A x_k^{(n)})$ converges rapidly to the exact value λ_k. In order to illustrate this, one may assume, without a loss of generality, that matrix A is a diagonal one. The solution may then be written down in the explicit form:

$$x_k^{(n)} = c_n \left[\left(\frac{\lambda_k - \mu}{\lambda_1 - \mu} \right)^n u_1, \ldots, u_k, \ldots, \left(\frac{\lambda_k - \mu}{\lambda_n - \mu} \right)^n u_n \right]^T. \tag{24}$$

It can be seen from Eq. (24) that all components of vector $x_k^{(n)}$ (except for u_k, which remains equal to unity) tend to zero under the given normalization conditions. Practical calculations demonstrate that this method is also the most resistant to rounding errors (calculation errors).

V. RESULTS AND DISCUSSION

In Table I we check the convergence of energy for the ground state of helium versus increasing basis sets of the variational expansion. The structure of "layers" of basis functions is very similar to what was used in our previous calculations [22], where it was explicitly published (see Table I in [22]). In the present case we optimized the variational basis with $N = 10\,000$ functions and eight layers. For the final calculation with $N = 22\,000$ functions we used 12 layers, and for the last four layers the ends of intervals $[A_1, A_2]$ and $[B_1, B_2]$ grew exponentially: $A_1(j) = B_1(j) = 10^{j-4}$, $A_2(j) = B_2(j) = 10^{j-3}$ for $j = 9, \ldots, 12$. Computations were performed in the

duodecimal arithmetics (about 100 decimal digits). Programs of duodecimal precision were developed by our group in order to overcome the problem of the numerical instability of calculations at large values of N.

The final results of numerical calculations of the ionization energies for S, P, D, and F states of a helium atom are presented in Table II. Variational parameters were optimized manually. It should be noted that the optimal variational parameters for different states differ significantly, and the calculation accuracy depends to a considerable extent (5–8 digits) on the particular choice of optimal variational parameters for a given bound state. Basis sets with $N = 10\,000$ functions were used to optimize the variational parameters. When the non-S states listed in the table were calculated, four to six "layers" of basis functions were used, while for the S states calculations were done in a similar way as for the ground state. The results in Table II are presented for two subsequent calculations with increasing basis sets, which allows us to demonstrate convergent digits. The third line shows the results of variational calculations by Drake and Yan [23] performed in the year 1992, where the Rydberg states (excluding S states) of helium were studied. Comparison between two calculations demonstrates excellent agreement. The largest set for each particular state has been chosen for the reason that further increase of the basis gives rise to numerical instability of calculations within given duodecimal arithmetics. As may be seen, numerical precision for triplet states is slightly higher, probably due to the smaller effect of the logarithmic singularity. For higher orbital angular momentum states we have managed to achieve precision of 27–28 digits. Still, that is the best-known data for these states. All the calculations were performed on the Linux mainframe computers of our laboratory.

For the ground-state energy we compare our best obtained value with previously published results in Table III. Indeed, explicit inclusion of the logarithmic singularity into a variational expansion may seriously improve precision of the results. On the other hand, with our variational basis function we can easily extend calculations to the states with excited electronic orbital as well as nonzero angular momentum states with large L.

TABLE IV. Convergence of the nonrelativistic energy of the H$^-$-ion ground state. Exponential variational expansion.

N	Energy (in a.u.)
14000	−0.52775 10165 44377 19659 08145 66747 2
18000	−0.52775 10165 44377 19659 08145 66747 55
22000	−0.52775 10165 44377 19659 08145 66747 576
26000	−0.52775 10165 44377 19659 08145 66747 5776

TABLE V. Comparison of nonrelativistic energies of the H^--ion ground state.

Author (year)	Ref.	N	Energy (in a.u.)
Morgan *et al.* (1990)	[9]	–	−0.52775 10165 44375
Drake *et al.* (2002)	[24]	2276	−0.52775 10165 44377 1965
Frolov (2006)	[25]	3700	−0.52775 10165 44377 19659 0
Nakashima, Nakatsuji (2007)	[26]	9682	−0.52775 10165 44377 19659 08145 66747 511
This work		26000	−0.52775 10165 44377 19659 08145 66747 5776

The last two Tables IV and V are devoted to the calculations of the single bound state in the negative hydrogen ion, H^-. In this case our numerical result for the energy is the most precise compared to previous calculations of this quantity. In the work of Nakashima and Nakatsuji [26], the data presented in Table V was claimed as convergent; presumably that indicates that the free iterative complement interaction method possesses some difficulties in the inner criterium to determine actual accuracy of the calculation.

Recently, we also studied applications of our method to the bound and resonant states in the hydrogen molecular ion H_2^+, which are supported by the ground electronic state $1s\sigma_g$ adiabatic potential [27]. All the states up to $v = 19$ vibration excited state and $L = 41$ rotational state were accessible for very high precision calculations. That gives yet another evidence of great universality of the variational exponential expansion.

VI. CONCLUSIONS

Variational wave functions of bound states are obtained by solving the Schrödinger equation for the quantum three-body problem with Coulomb interaction using a variational approach based on exponential expansion with the parameters of exponents being chosen in a pseudorandom way. The results of these studies demonstrated that the energy values were accurate to 27–35 significant digits. We obtained the most accurate value in the case of the negative hydrogen ion H^- ground state as compared to the published data.

ACKNOWLEDGMENTS

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