Optimization of nonlinear parameters in trial wave functions with a very large number of terms

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A procedure is proposed to construct highly accurate variational wave functions with large and very large numbers of basis functions. The procedure has a number of advantages in actual computations on parallel computer clusters. In particular, by using this procedure we have determined very accurate numerical values of the ground-state energies in the positronium ion Ps$^-$ (or $e^- e^+ e^-$) ($E = -0.262\,005\,070\,232\,980\,107\,770\,375$ a.u.) and hydrogen ion $^\infty$H$^-$ ($E = -0.527\,751\,016\,544\,377\,196\,589\,759$ a.u.) The variational energies of the negative hydrogenlike ions (or H$^-$-like ions) with the finite nuclear masses (T$^-$, D$^-$, ^{1}H$^-$, and Mu$^-$) are also presented. These energies are the best variational ground-state energies ever obtained for these ions.

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In our work [1], we proposed a very effective strategy for constructing highly accurate, variational wave functions. Later, the procedure from [1] was applied to dozens of Coulomb and non-Coulomb three-body systems. Based on the procedure in [1], we have achieved significant progress in highly accurate computations of various few-body and three-body systems. In this study, we improve the optimization strategy proposed in [1] by adding one additional and very important step that allows us to increase (drastically) the overall quality of the method. In particular, this step is needed to construct the optimal wave functions with large and extremely large numbers of basis functions.

The improved strategy works for an arbitrary three-body system. However, bearing in mind the importance of the hydrogenlike negatively charged ions for numerous applications (see, e.g., [2]), below we want to apply the newly developed strategy to construct highly accurate wave functions for the $^\infty$H$^-$ ion and for a few other similar systems. Also in this study we consider the ground 1 ^1S ($L=0$) states in the similar two-electron positronium ion Ps$^-$ (or $e^- e^+ e^-$) and muonic ion Mu$^-$ (or $e^- \mu^+ e^-$). For hydrogenlike ions with finite nuclear masses, e.g., for ^{1}H$^-$, D$^-$, and T$^-$ ions, we take into account the recent nuclear masses recommended by NIST [3]. Note that the bound states in these ions cannot be considered with the use of the Hartree-Fock method because it does not produce any bound states in these ions.

Our main computational goal below is to solve the corresponding Schrödinger equation $H\Psi = E\Psi$, where H is the Hamiltonian, $E < 0$ is the bound-state energy, and Ψ is the corresponding three-body wave function. As is well known (see, e.g., [4]) for the bound-state spectra, this problem is equivalent to the optimization or minimization of the energy functional, i.e.,

$$H\Psi = E\Psi \Leftrightarrow E = \min_\Psi \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \qquad (1)$$

In actual applications, the unknown wave function Ψ is represented by the linear combinations of some basis functions ϕ_i, i.e., $\Psi = \Sigma_{i=1}^N C_i \phi_i$, where the coefficients C_i are the linear (or variational) parameters of the method. In such cases, the

problem, Eq. (1), is reduced to a solution of the following eigenvalue problem:

$$(\hat{H} - E \cdot \hat{S})\mathbf{C} = 0 \Rightarrow (\hat{D}^{-1/2} \hat{U} \hat{H} \hat{U}^{-1} \hat{D}^{-1/2} - E)\mathbf{C} = 0, \qquad (2)$$

where $\hat{U}$ is the unitary matrix that reduces the overlap matrix ($\hat{S}$) to the diagonal form $\hat{D}$, i.e., $\hat{S} = \hat{U}^{-1} \hat{D} \hat{U}$. In many applications, the Hamiltonian matrix $\hat{H}$ and the overlap matrix $\hat{S}$ are two dense matrices of large ($N \geq 2500$) and very large ($N \geq 4000$) dimensions. An accurate solution (and even a partial solution) of Eq. (2) is a very complicated problem. The main problem is related to the fact that the Hamiltonian matrix $\hat{H}$ and overlap $\hat{S}$ matrix in Eq. (2) are extremely ill-conditioned, i.e., almost degenerated. In particular, the condition number K [5] for a typical overlap matrix in our present computations was $K = \log_{10}(|\lambda_{max}(S)|/|\lambda_{min}(S)|) \approx 75-110$, where $\lambda_{max}(S)$ and $\lambda_{min}(S)$ are the maximal and minimal eigenvalues of the overlap matrix $\hat{S}$ (in fact, all eigenvalues of any overlap matrix are always positive). In addition to very large condition numbers, in actual cases each matrix element of these matrices depends on some nonlinear parameters that must be optimized to determine the lowest possible energy E.

In actual computations, all of these trouble spots can be avoided with the use of extended arithmetic accuracy. The most effective FORTRAN-based packages with arbitrary arithmetic precision have been written and extensively tested by Bailey [6,7]. This extended precision software works very effectively in applications to various few-body systems. Note that in our present computations we operated with computer words that contain from 80 up to 116 decimal digits.

In fact, in this study we restrict ourselves to the consideration of the ground 1 ^1S ($L=0$) states in the symmetric Coulomb three-body systems only. Below, we determine the energies and other bound-state properties of the ground 1 ^1S ($L=0$) states in the Ps$^-$ (or $e^- e^+ e^-$) and $^\infty$H$^-$ ions by using our optimization strategy for the nonlinear parameters in the trial wave functions. The Hamiltonian H for each of these Coulomb three-body systems takes the following form (in atomic units $\hbar = 1$, $m_e = 1$, $e = 1$):

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2M}\nabla_3^2 - \frac{1}{r_{32}} - \frac{1}{r_{31}} + \frac{1}{r_{21}}, \qquad (3)$$

where M is the mass of the positive particle in the ions considered, i.e., $M=1$ for the Ps$^-$ ion and $M=\infty$ for the $^\infty$H$^-$ ion. The operator $\nabla_i = (\partial/\partial x_i, \partial/\partial y_i, \partial/\partial z_i)$ is the three gradient operators ($i=1,2,3$), while $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$ are the three relative coordinates [here and below $(ij) = (21),(31),(32)$]. Also, in this equation and everywhere else herein, the subscripts 1 and 2 stand for the electrons e^-, while the subscript 3 means the positively charged particle, i.e., positron e^+ in the Ps$^-$ ion and infinitely heavy nucleus in the $^\infty$H$^-$ ion. As mentioned above, our present goal is to determine the highly accurate solutions of the corresponding Schrödinger equation $H\Psi = E\Psi$, where $E < 0$.

The exact wave functions of the Ps$^-$ and H$^-$ ions are approximated with the use of exponential variational expansion in relative or perimetric coordinates r_{32}, r_{31}, r_{21} and u_1, u_2, u_3, respectively. For the ground $1\,^1S$ states in the Ps$^-$ and H$^-$ ions, this expansion takes the form [1]

$$\Psi = \frac{1}{2}(1 + \hat{P}_{21}) \sum_{i=1}^{N} \widetilde{C}_i \exp(-\widetilde{\alpha}_i r_{32} - \widetilde{\beta}_i r_{31} - \widetilde{\gamma}_i r_{21})$$

$$= \frac{1}{2}(1 + \hat{P}_{21}) \sum_{i=1}^{N} C_i \exp(-\alpha_i u_1 - \beta_i u_2 - \gamma_i u_3). \qquad (4)$$

Here C_i are linear (or variational) parameters and $\alpha_i(\widetilde{\alpha}_i)$, $\beta_i(\widetilde{\beta}_i)$, and $\gamma_i(\widetilde{\gamma}_i)$ are nonlinear parameters. The operator $\hat{P}_{21}$ is the permutation of the two identical (1 and 2) particles (electrons) in the Ps$^-$ and H$^-$ ions. The perimetric coordinates u_1, u_2, u_3, in Eq. (4) are simply related to the three relative coordinates r_{32}, r_{31}, r_{21}: $r_{ij} = u_i + u_j$ and vice versa $u_i = \frac{1}{2}(r_{ki} + r_{ij} - r_{kj})$, where $i \neq j = (1,2,3)$ and $r_{ij} = r_{ji}$. Therefore, for the nonlinear parameters α_i, β_i, and γ_i in Eq. (4) one finds $\gamma_i = \widetilde{\alpha}_i + \widetilde{\beta}_i$, $\beta_i = \widetilde{\alpha}_i + \widetilde{\gamma}_i$, and $\alpha_i = \widetilde{\gamma}_i + \widetilde{\beta}_i$. Since the perimetric coordinates u_1, u_2, u_3 are truly independent and always positive, all nonlinear parameters α_i, β_i, and γ_i($i = 1, \dots, N$) in Eq. (4) are also positive. This fact significantly simplifies their optimization. In contrast with this some of the nonlinear parameters, $\widetilde{\alpha}_i, \widetilde{\beta}_i, \widetilde{\gamma}_i$ ($i = 1, \dots, N$) can be negative and, therefore, their optimization is not an easy task.

The optimization strategy used in this study is essentially based on the procedure developed in our earlier work [1]. That procedure [1] allows one to construct extremely accurate wave functions of very high quality for an arbitrary three-body system. In general, the procedure [1] includes the following two steps. For many systems, the first step is the construction of the short-term cluster functions with $N \approx 400-600$ basis functions [1]. All nonlinear parameters ($\approx 1200-1800$ parameters) in such wave functions are carefully optimized. Recently, such "well optimized" short-term wave functions have been constructed for all important three-body systems.

At the second step, our goal is to construct the many-term part of the trial wave function, which usually includes 1000–2500 basis functions (long-term tail of the wave function). The number of nonlinear parameters in such cases is too

large (≥ 5000) to be optimized carefully. Therefore, some different strategies must be applied in those cases when $N \geq 1000$. In fact, the nonlinear parameters in the wave functions are chosen quasirandomly from 3, 4,…, 10 different parallelotopes or boxes [1]. The sizes and relative positions of these boxes are the real nonlinear parameters of the method [1]. In the case of the three-box version, one finds 28 actual nonlinear parameters [1]. All of these 28 parameters can be optimized quite accurately, if the total number of basis functions $N \leq 2500$. Then the total number of the basis function is increased to larger values, e.g., $N=3500$ and/or $N=4200$. The nonlinear parameters are not changed during this last step of the procedure.

Recently, however, it was found in computations that the optimal values of nonlinear parameters determined, e.g., for $N=2500$, are not even close to the optimal values of these parameters obtained for $N \geq 3500$, i.e., the overall quality of the wave function with $N \geq 3500$ terms is certainly not very good. But how can we improve the overall accuracy of the wave function in those cases when $N \geq 3500$? It is clear that the reoptimization of all 28 nonlinear parameters for $N \approx 3500$ cannot be used, in principle, since such a process takes a very long time. The only working strategy at such dimensions is to reduce the total number of actual nonlinear parameters. The further study of this problem shows that not all 28 nonlinear parameters are equally important in computations with large N. In general, among 28 nonlinear parameters one always finds the three following groups of parameters: (i) a group of rapidly changing parameters (the optimization of each of these parameters produces a significant decrease in the total energy), (ii) slowly changing parameters (relatively small changes in the total energy), and (iii) unimportant parameters (their optimization provides just very small changes in the total energy or no changes at all). As follows from the results of numerous computations at large dimensions, approximately 1/3 of all nonlinear parameters at large dimensions are rapid (or fast) parameters, while $\approx 1/3$ of them are slow varying parameters and the remaining 1/3 of these parameters are nonimportant parameters. From computations of various systems with $N=3500-4200$ basis functions, we have observed the following combinations: 10-10-8, 11-9-8, 9-10-9, etc. Here we assume that the total number of nonlinear parameters equals 28, and the notation $a-b-c$ means the combination of a fast, b slow, and c unimportant nonlinear parameters.

It is clear that the direct selection of fast parameters at very large dimensions is also a very complicated and costly problem. However, in most cases the nonlinear parameters, which were found to be fast in computations with $N=2500$ basis functions, are also fast parameters in computations with $N=3500$ basis functions. In general, only a very few nonlinear parameters may change their type when N increases from 2500 to 3500 and higher values. A typical situation is, e.g., when one fast parameter for $N=2500$ becomes a slow parameter for $N=3500$ and/or one slow parameter changes to an unimportant parameter, etc. However, a substantial part of the nonlinear parameters do not change their type when N increases from 2500 to 3500–4000 basis functions. This fact follows from the results of numerous computations with large and very large numbers of basis functions. Finally, the

TABLE I. The total energies (E) in atomic units ($m_e=1$, $h=1$, $e=1$) for the ground states of the Ps$^-$ and H$^-$ ions. N designates the number of basis functions used.

N	$E(\text{Ps}^-)$	N	$E(^\infty\text{H}^-)$
3000	$-0.26200\ 50702\ 32980\ 10777\ 0054$	2800	$-0.52775\ 10165\ 44377\ 19658\ 8192$
3300	$-0.26200\ 50702\ 32980\ 10777\ 0204$	3000	$-0.52775\ 10165\ 44377\ 19658\ 8632$
3500	$-0.26200\ 50702\ 32980\ 10777\ 0262$	3300	$-0.52775\ 10165\ 44377\ 19658\ 9134$
3700	$-0.26200\ 50702\ 32980\ 10777\ 0293$	3500	$-0.52775\ 10165\ 44377\ 19658\ 9410$
3800	$-0.26200\ 50702\ 32980\ 10777\ 0301$	3700	$-0.52775\ 10165\ 44377\ 19658\ 9586$
3800[a]	$-0.26200\ 50702\ 32980\ 10777\ 0375$	3700[a]	$-0.52775\ 10165\ 44377\ 19658\ 9759$
E^b [6]	$-0.26200\ 50702\ 32980\ 10776\ 886$	E^b	$-0.52775\ 10165\ 44377\ 19658\ 67$
E^b [5]	$-0.26200\ 50702\ 32980\ 10769\ 6$	E^b	$-0.52775\ 10165\ 44377\ 19650\ 3$
E^b [4]	$-0.26200\ 50702\ 3294$	E^b	

[a]Additional optimization of the fast nonlinear parameters at this dimension has been used.
[b]The best variational energies (in a.u.) know for these ions from earlier calculations.

fast nonlinear parameters (selected at smaller dimensions) are approximately optimized at large and very large dimensions. By using a few parallel computer clusters, one can optimize some or all fast parameters at one step. This procedure allows one to obtain the variational energies and other bound state properties, which are significantly more accurate than analogous energies or properties known from "regular" calculations based on our earlier strategy [1]. The results from Table I show that even approximate optimization of the fast nonlinear parameters at large or maximal dimensions produces better (=lower) variational energies than careful and accurate optimization of all such parameters at smaller dimensions.

To illustrate the abilities of this method in actual computations in this study, we determine the ground-state energies of the Ps$^-$ and $^\infty$H$^-$ ions. The variational energies of these ions determined with the exponential variational wave functions, Eq. (4), are presented in Table I. Note that these energies are significantly more accurate than the energies obtained for these systems in all earlier works, including a few of ours. Table I also contains the variational results obtained for these two-electron ions in earlier works [8–10]. More references for these ions prior to 2002 can be found, e.g., in [9]. Table II contains the variational energies of the different H$^-$-like ions with the finite nuclear masses. In fact, the T$^-$, D$^-$, ^{1}H$^-$, and Mu$^-$ (=$\mu^+ e^- e^-$) ions are presented in this Table. In our present calculations, we have used the following particle masses: $m_t=5496.921\ 58 m_e$, $m_d=3670.482\ 965\ 2 m_e$, $m_p=1836.152\ 672\ 61 m_e$, and $m_\mu=206.768\ 284 m_e$ [3]. These masses are currently recommended by NIST [3] and they are

slightly different from the values that we have used in our earlier computations of these ions (except for the value of the tritium mass). The determined ground-state energies indicate clearly that the optimization strategy developed in this study has a great potential for highly accurate computations of the bound-state spectra in various three-body systems.

In conclusion, we want to note that the highly accurate energies determined for all three-body ions considered in this study are of some interest in a number of applications. However, in many cases some bound-state properties of these ions are of much greater interest. In this work, these properties have also been determined to a very good accuracy, but many of them are in very good agreement with the values obtained in our earlier work [10]. Therefore, it is not necessary to present all of them here. Let us report only our best expectation values for the electron-positron, electron-electron, and triple-δ functions in the Ps$^-$ ion: $\langle \delta_{+-} \rangle = 2.073\ 319\ 800\ 518\ 3 \times 10^{-2}$, $\langle \delta_{--} \rangle = 1.709\ 967\ 563\ 596 \times 10^{-4}$, and $\langle \delta_{+--} \rangle = 3.588\ 915\ 8 \times 10^{-5}$ (all values are in atomic units). The first and last of these expectation values determine different annihilation rates of the positron ($\Gamma_{2\gamma}$, $\Gamma_{3\gamma}$, $\Gamma_{4\gamma}, \ldots$ and $\Gamma_{1\gamma}$, respectively) in the Ps$^-$ ion. In particular, by using our $\langle \delta_{+-} \rangle$ and $\langle \delta_{+--} \rangle$ expectation values and formulas from [10], one finds $\Gamma_{2\gamma} \approx 2.080\ 485\ 305\ 25 \times 10^9$ s^{-1}, $\Gamma_{3\gamma} \approx 5.636\ 415\ 155\ 0 \times 10^6$ s^{-1}, and $\Gamma_{1\gamma} \approx 3.824\ 91 \times 10^{-2}$ s^{-1}. The agreement with the $\Gamma_{1\gamma}$ value obtained in [10] can be considered to be very good (this expectation value contains the triple-δ function $\langle \delta_{+--} \rangle$, which is not easy to evaluate due to its very slow convergence rate).

TABLE II. The total energies (E) in atomic units for the ground $1\ ^1S$ ($L=0$) states of some H$^-$-like ions. N designates the number of basis functions used.

Ion	N	E	Ion	N	E
T$^-$	2800	$-0.52764\ 90482\ 02999\ 95037\ 3116$	^{1}H$^-$	2800	$-0.52744\ 58811\ 09463\ 97978\ 5780$
T$^-$	3700	$-0.52764\ 90482\ 02999\ 95037\ 5038$	^{1}H$^-$	3700	$-0.52744\ 58811\ 09463\ 97978\ 7790$
D$^-$	2800	$-0.52759\ 83246\ 84448\ 42166\ 8461$	Mu$^-$	2800	$-0.52505\ 48065\ 28795\ 36587\ 1114$
D$^-$	3700	$-0.52759\ 83246\ 84448\ 42167\ 0480$	Mu$^-$	3700	$-0.52505\ 48065\ 28795\ 36587\ 2993$

Note also that the expression for the two-photon annihilation rate $\Gamma_{2\gamma}$, used in [10], also includes the lowest-order radiative correction to the two-photon annihilation rate [11]. The sum of the $\Gamma_{2\gamma}$ and $\Gamma_{3\gamma}$ annihilation rate is called the total annihilation rate $\Gamma \approx 2.086\,121\,720\,4 \times 10^9$ s^{-1}. The known experimental value of the total annihilation rate Γ for the Ps$^-$ ion is $2.09(9) \times 10^9$ s^{-1} [12]. The detailed study of positron annihilation in the Ps$^-$ ion will be considered elsewhere.

Thus, the newly developed optimization strategy for the wave functions with the large and very large numbers of nonlinear parameters allows one to produce extremely accurate (or essentially exact) variational wave functions for an arbitrary three-body systems. Currently, the overall accuracy of our three-body wave functions is far beyond the analogous numerical accuracy that can be provided by any alternative three-body method. These wave functions can now be used to determine (to very high accuracy) the expectation values of all regular and most singular properties in arbitrary three-body systems. In particular, the newly constructed wave functions can be applied to obtain the lowest-order relativistic and QED corrections in the Ps$^-$, Mu$^-$, ^{1}H$^-$, D$^-$, T$^-$, and $^\infty$H$^-$ ions and other two-electron ions and atoms.

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