Two-stage strategy for high-precision variational calculations

Alexei M. Frolov
Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6
(Received 15 October 1997)

The problem of high-precision, variational, bound-state calculations in few-body systems is discussed. The simple and very effective variational procedure developed below makes possible numerical, bound-state computations in few-body systems with extremely high accuracy. This procedure is based on the proposed two-stage strategy, which is used to construct the approximate wave function. The highly accurate numerical results, which include both energetical and geometrical properties, for various three-body systems [Ps^-,$^\infty H^-$,$^\infty$He, and $(ppe)^+$] are presented. [S1050-2947(98)01704-1]

PACS number(s): 31.25.−v, 36.10.Dr

In the present communication we discuss the problem of high-precision variational calculations to determine the bound states in few-body systems. Our main goal is to improve significantly the methods that are used so far for such calculations. The key to this problem is the use of the two-stage procedure to construct extremely accurate trial wave functions. Let us consider the variational expansion for the trial wave function Ψ, which contains N terms or basis functions. Presently, we shall assume that each of these basis functions (1) contains the same number of nonlinear parameters k, and (2) has the correct asymptotic behavior in each of the system's decay channels. Actually, this means that we consider the so-called fast convergent variational expansions, and furthermore, such a convergence is observed not only for the total energies, but also for all other properties [1].

In the proposed two-stage procedure the trial wave function Ψ is represented by the sum of the very well optimized, short-term function Ψ_1 and roughly optimized (or even nonoptimized), long-term function Ψ_2. If the total number of terms equals N, then we may write $\Psi(N)=\Psi_1(N_0)+\Psi_2(N-N_0)$, where $N_0 \ll N$. In terms of the first assumption made above, the $\Psi_1(N_0)$ function includes kN_0 nonlinear parameters, while the $\Psi_2(N-N_0)$ function contains $k(N-N_0)$ such parameters. Correspondingly, the first stage of the procedure is to optimize quite well only the kN_0 nonlinear parameters, which is significantly smaller than the total number of these parameters (kN) in the trial wave function Ψ. In the second stage the total number of nonlinear parameters grows extensively, but they can be chosen with, roughly, optimization or even without optimization, e.g., in a regular [2] or quasirandom manner (see, e.g., [3] and references therein). As is shown below, the first stage produces a very compact and highly accurate wave function Ψ_1. The appropriate energy contains approximately 10–12 correct decimal figures (in the atomic units). The second stage gives as a rule 2–3 additional correct decimal figures to the total energy, and generates the extremely accurate wave function, which can be used to compute the various properties in the considered system.

In order to make the discussion clearer and more concrete we restrict ourselves in this study to consideration of the Coulomb three-body systems only. Moreover, only the exponential variational expansion in the relative coordinates is used below. In the general case it takes the form [3]

$$\Psi_{LM}=\frac{1}{2}(1+\kappa\hat{P}_{21})\sum_{i=1}^{N}\sum_{\ell_1=\epsilon}^{L} C_i \mathcal{Y}_{LM}^{\ell_1,\ell_2}(\mathbf{r}_{31},\mathbf{r}_{32})\exp(-\alpha_i r_{32} - \beta_i r_{31}-\gamma_i r_{21})\exp(\imath\delta_i r_{32}+\imath e_i r_{31}+\imath f_i r_{21}), \quad (1)$$

where C_i are the linear (or variational) parameters, α_i, β_i, γ_i, δ_i, e_i, and f_i are the nonlinear parameters. The functions $\mathcal{Y}_{LM}^{\ell_1,\ell_2}(\mathbf{r}_{31},\mathbf{r}_{32})$ are the so-called Schwartz [4] or bipolar harmonics. The operator P_{21} is the permutation of the identical particles in the symmetric systems, where $\kappa=+1$ (or -1), otherwise $\kappa=0$. Actually, in the present study we consider the symmetric systems with $\kappa=+1$, and with the zero value of the total angular momentum $L=0$, i.e., the ^1S states. The ground states in these systems are of specific interest, since they were intensively studied previously, and a large number of quite accurate results have been reported for them (see, e.g., [3,5–12]).

It should be mentioned here that the exponential variational expansion Eq. (1) was used successfully to solve a wide number of complicated problems. The present form Eq. (1) corresponds to the universal variational expansion for three-body systems [3]. This means that Eq. (1) can be applied directly for highly accurate bound-state calculations in arbitrary three-body systems, including the so-called adiabatic case when $\min(m_1,m_2)\gg m_3$ and $q_1q_2>0$ (for more detail see [3]). Presently, we consider the four following systems: the $Ps^-(e^-e^+e^-)$ and $^\infty H^-$ ions, the $^\infty$He atom and the $(ppe)^+$ molecular ion. The last system is certainly adiabatic, since $m_p=1836.152701m_e\gg m_e$ [13]. The wave function is taken to be real ($\delta_i=e_i=f_i=0$, for $i=1,\ldots,N$) for all the systems except the almost-adiabatic case $^1H_2^+$ (or ppe^+), where all the nonlinear parameters are retained.

Now, the principal problem is to find an optimal strategy how to choose the nonlinear parameters in Eq. (1). In many previous works the nonlinear parameters $\alpha_i,\beta_i,\gamma_i$ or $\alpha_i,\beta_i,\gamma_i,\delta_i,e_i,f_i$, where $i=1,2,\ldots,N$, in Eq. (1) were generated in a quasirandom manner (for details and references see, e.g., [3]) from the three or six real intervals, respectively. In particular, this approach was intensively used in our previous studies (see, e.g., [3,14] and references therein). It works quite well, but the competing approach improved recently [5,6] provides a better accuracy. The two-stage procedure stated in this work eliminates completely the

TABLE I. The total energies (E) in atomic units ($m_e=1,\hbar=1,e=1$) for the ground states of some three-body systems. N designates the number of basis functions used.

N	E [a] (Ps^-)	N	E [a] ($^\infty H^-$)	N	E [a] ($^\infty He$)	N	$E((ppe)^+)$
200	-0.262005070222620	200	-0.527751016541252	200	-2.903724377031417	100	-0.5971390322825
400	-0.262005070231129	300	-0.527751016541986	300	-2.903724377032210	200	-0.5971390492823
500	-0.262005070232527	400	-0.527751016543162	400	-2.903724377033432	250	-0.5971390568858
600	-0.262005070232785	500	-0.527751016543794	500	-2.903724377033841	300	-0.5971390611207
700	-0.262005070232898	600	-0.527751016544057	600	-2.903724377033992	350	-0.5971390625299
800	-0.262005070232942	700	-0.527751016544195	700	-2.903724377034051	400	-0.5971390629722
900	-0.262005070232957	750	-0.527751016544233	800	-2.903724377034080	450	-0.5971390630813
950	-0.262005070232961	775	-0.527751016544243	825	-2.903724377034086	475	-0.5971390630895
1000	-0.262005070232965	800	-0.527751016544253	850	-2.903724377034091	500	-0.5971390631031

[a]The best variational results for these systems are -0.26200507023296538 a.u., -0.52775101654425325 a.u., and -2.9037243770340913 a.u., respectively. In Table I only 15 significant decimal figures after the comma are given for each energy.

accuracy problem from bound-state calculations, since it can be made, in principle, arbitrarily high. Our present results show how this strategy works for the four systems mentioned above. The two following values of N_0 and N have been used in the present study: $N_0=200$ in all cases and $N=800-1000$. Note that the actual numbers of basis functions used in the $(ppe)^+$ calculations were twice less in each case, i.e., $N_0=100$ and $N=500$, respectively.

The found variational energies are presented in Table I. In both Tables I and II only atomic units are used: $m_e=1$, $e=1$, and $\hbar=1$. The results for $N=200(=N_0)$ correspond to the highly accurate short-term wave function Ψ_1. These functions and their improved versions can be found elsewhere [15] and everyone may use them in his own calculations. Note only, that the Ps^-, $^\infty H^-$ and $^\infty He$ wave functions Ψ_1 contains 600 nonlinear parameters each, while the $(ppe)^+$ wave function includes 1200 such parameters [16]. The choice of the nonlinear parameters corresponds to the wave function represented explicitly in the form Eq. (1). As follows from Table I the final accuracy for the total energies E achieved by using the proposed two-stage approach is higher than known from the previous works. But it is probably more important to note that such an accuracy can be increased significantly by performing better optimization for the short-term Ψ_1 function [15].

The numerical values for some of the properties (i.e., expectation values) are presented in Table II. The physical meaning for almost all of these expectation values is quite clear from the notations used, and here we can make only a few following remarks. In all the formulas given below the notations 1 and 2 mean the two identical particles, while the notation 3 designates the different one. δ_{31},δ_{21}, and δ_{321} stand for the two- and three-particle Dirac δ functions, respectively. The two-body cusp ratios are determined in a traditional manner:

$$\nu_{ij}=\frac{\left\langle \delta(\mathbf{r}_{ij})\frac{\partial}{\partial r_{ij}}\right\rangle}{\langle\delta(\mathbf{r}_{ij})\rangle}, \tag{2}$$

where $\delta_{ij}=\delta(\mathbf{r}_{ij})$ is the appropriate Dirac δ function and $(ij)=(21)$ and (31). The exact value of ν_{ij} equals [17]

$$\nu_{ij}=q_iq_j\frac{m_im_j}{m_i+m_j} \tag{3}$$

where q_i and q_j are the charges and m_i and m_j the masses of the particles.

The expectation values of the two interparticle *cosine* functions are determined traditionally:

$$\tau_{ij}=\langle\cos(\mathbf{r}_{ik}\times\mathbf{r}_{jk})\rangle=\left\langle\frac{\mathbf{r}_{ik}\cdot\mathbf{r}_{jk}}{r_{ik}r_{jk}}\right\rangle, \tag{4}$$

where $(i,j,k)=(1,2,3)$. The quantity $\langle f\rangle$ is expressed in terms of the relative coordinates (r_{31},r_{32},r_{21}) or perimetric coordinates (u_1,u_2,u_3) [where $u_i=\frac{1}{2}(r_{ij}+r_{ik}-r_{jk})$, and $(i,j,k)=(1,2,3)$] as follows:

$$\langle f\rangle=\left\langle\psi\left|\frac{u_1}{r_{32}}\frac{u_2}{r_{31}}\frac{u_3}{r_{21}}\right|\psi\right\rangle$$
$$=\int\int\int|\psi(u_1,u_2,u_3)|^2u_1u_2u_3du_1du_2du_3. \tag{5}$$

The value $\langle f\rangle$ can be calculated directly or by applying τ_{ij}. The equalities

$$\tau_{21}+\tau_{32}+\tau_{31}=1+4\langle f\rangle \quad\text{and}\quad \tau_{21}+2\tau_{31}=1+4\langle f\rangle \tag{6}$$

hold for arbitrary three-body nonsymmetric and symmetric $(1\Leftrightarrow2)$ systems, respectively. The virial factor η is determined as follows:

$$\eta=\left|1+\frac{\langle V\rangle}{2\langle T\rangle}\right|, \tag{7}$$

where $\langle T\rangle$ and $\langle V\rangle$ are the expectation values of the kinetic and potential energy, respectively. The deviation of the factor η from zero indicates the quality of the wave function used. The appropriate binding energies ε are given in eV (1 Ry = 27.2113961 eV). Note also that in Table II only stable figures from calculations with the higher values of N are presented. It follows from Table II that all previous problems related with slow convergence for some expectation values (e.g., for the $\langle r_{21}^4\rangle$ or $\langle\nabla_1\cdot\nabla_3\rangle$ values) are solved successfully by applying the highly accurate wave functions. However, analogous problems for the $\langle\delta_{21}\rangle,\langle\delta_{321}\rangle$, and ν_{21}

TABLE II. The expectation values $\langle X_{ij}\rangle$ in atomic units ($m_e=1,\hbar=1,e=1$) of some properties for the ground states in some three-body systems.

$\langle X_{ij}\rangle$	Ps^-	$^{\infty}H^-$	$^{\infty}He$	$(ppe)^+$
$\langle r_{21}^{-2}\rangle$	0.03602205849	0.15510415296	1.4677092349	1.425744903
$\langle r_{31}^{-2}\rangle$	0.279326542159	1.1166628242	6.0174088662	0.2439234991
$\langle r_{21}^{-1}\rangle$	0.155631905653	0.31102150222	0.945818448800	0.49070779859
$\langle r_{31}^{-1}\rangle$	0.339821023059	0.68326176765	1.688316800717	0.84249296238
$\langle r_{21}\rangle$	8.54858065512	4.4126944977	1.422070255566	2.0639138675
$\langle r_{31}\rangle$	5.48963325237	2.7101782783	0.929472294874	1.69296620840
$\langle r_{21}^{2}\rangle$	93.178633857	25.202025295	2.516439312836	4.3132859444
$\langle r_{31}^{2}\rangle$	48.418937230	11.913699680	1.193482995021	3.5587979296
$\langle r_{21}^{3}\rangle$	1265.5804489	180.6056011	5.30800964084	9.125657555
$\langle r_{31}^{3}\rangle$	607.29563013	76.02309752	1.96794810670	8.709881574
$\langle r_{21}^{4}\rangle$	21054.45349	1590.094673	12.981271359	19.54234939
$\langle r_{31}^{4}\rangle$	9930.638730	645.1445780	3.9735649319	24.034835140
$\langle (r_{31}\cdot r_{32})^{-1}\rangle$	0.090935346529	0.382627890321	2.70865547443	0.607695916941
$\langle (r_{31}\cdot r_{21})^{-1}\rangle$	0.060697690289	0.253077567089	1.92094392188	0.416234396614
τ_{31}	0.591981701149	0.649871581195	0.648017667474	0.509967771935
τ_{21}	0.019769632817	-0.105147693565	-0.064202614219	0.251989492715
$\langle f\rangle$	0.0509332587788	0.048648867206	0.0579581801820	0.0679812591465
$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{32}\rangle$	1.8296203020	-0.6873129673	-0.064736661397	1.40215495740
$\langle \mathbf{r}_{31}\cdot\mathbf{r}_{21}\rangle$	46.589316928	12.601012647	1.258219656418	2.15664297222
$\langle \frac{1}{2}\nabla_1^2\rangle$	0.0666192945359	0.2638755082723	1.451862188517	2.6133703465
$\langle \frac{1}{2}\nabla_3^2\rangle$	0.1287664811612	0.5606307983969	3.062793852119	0.594292491164
$\langle \nabla_1\cdot\nabla_2\rangle$	-0.004472107911	0.032879781851	0.159069475085	[b]
$\langle \nabla_1\cdot\nabla_3\rangle$	-0.063265213603	-0.288535344660	-1.571164294831	[b]
$\langle \delta_{31}\rangle$	0.0207331980	0.164552868	1.81042929	0.206736364
$\langle \delta_{21}\rangle$	0.17099699×10^{-3}	0.27379944×10^{-2}	0.106345374	0.444×10^{-9}
$\langle \delta_{321}\rangle$	0.358685×10^{-4}	0.506351×10^{-2}	1.868599	0.304×10^{-9}
ν_{31}	-0.4999997640218	-0.999998969784	-1.99999875493	-0.9994517779
ν_{31}^{a}	-0.5	-1.0	-2.0	-0.9994556794329
ν_{21}	0.499972144320	0.499980229939	0.499999799897	-100.0880
ν_{21}^{a}	0.5	0.5	0.5	918.0763505000
η	4.690×10^{-14}	3.093×10^{-12}	2.668×10^{-14}	2.816×10^{-11}
ε	-0.32667472131754	-0.75514390336334	-24.5916019887004	-2.65069538416

[a]The exact value from Eq. (2).
[b]These values were not computed.

values still remain, and for the adiabatic system $(ppe)^+$ such problems take a very complicated form (see Table II).

By using the expectation values given in Table II one may calculate a wide number of observable properties for these systems. For instance, the total and one-photon annihilation rates in the Ps^- ion can be found from the two following expressions [18,19]:

$$\Gamma = 2\pi\alpha^4 c a_0^{-1}\left[1-\alpha\left(\frac{17}{\pi}-\frac{19\pi}{12}\right)\right]\langle\delta_{31}\rangle$$
$$= 100.6174809\times10^9\langle\delta_{31}\rangle \ \ \mathrm{sec}^{-1}$$

$$\Gamma_{1\gamma}=\frac{4}{9}\frac{16\pi^2}{3}\alpha^8 c a_0^{-1}\langle\delta_{321}\rangle = 1065.75744\langle\delta_{321}\rangle \ \ \mathrm{sec}^{-1}, \quad (8)$$

where $\alpha=0.729735308\times10^{-2}$ is the fine structure constant, $c=0.299792458\times10^9$ m sec^{-1} is the velocity of light, and the Bohr radius a_0 equals $0.529177249\times10^{-10}$ m [20]. Now, by applying the expectation values for the appropriate Dirac δ functions from Table II one finds from the last equalities: $\Gamma=2.086122154\times10^9$ sec^{-1} and $\Gamma_{1\gamma}=3.82271\times10^{-2}$ sec^{-1}. The other annihilation rates $\Gamma_{2\gamma},\Gamma_{3\gamma},\ldots$ can be easily estimated by using the $\langle\delta_{31}\rangle$ value and formulas from [19].

Thus, in the present work a simple and very effective procedure was proposed to perform high-precision, variational, bound-state calculations in few-body systems. In particular, the three-body case is studied in detail, and it is shown that the high-precision expansions for the actual wave functions in arbitrary three-body systems can be made sig-

nificantly more compact than the expansions used so far. Furthermore, the developed two-stage strategy to choose the nonlinear parameters in the wave function is quite effective and can be applied to increase the final accuracy considerably [21].

ACKNOWLEDGMENTS

I wish to thank Professor V.H. Smith, Jr. for useful references and the Natural Sciences and Engineering Research Council of Canada for financial support.

[1] This remark is very important, since otherwise, by using a huge number of incorrect basis functions (e.g., ''cutted'' polynomials, many-dimensional gaussoids, etc.) with a large number of nonlinear parameters, one may decrease the total energy to very low values. In terms of the variational principle this means an obvious improvement of the wave function. But in general, the quality of such a wave function will remain poor. In particular, they are useless, as a rule, in actual calculations of many properties.
[2] L. M. Delves and T. Kalotas, Aust. J. Phys. **21**, 1 (1968).
[3] A. M. Frolov and V. H. Smith, Jr., Phys. Rev. A **49**, 3580 (1994); J. Phys. B **28**, L449 (1995).
[4] C. L. Schwartz, Phys. Rev. **123**, 1700 (1961).
[5] G. W. F. Drake, Nucl. Instrum. Methods Phys. Res. B **31**, 7 (1988).
[6] Y. K. Ho, Phys. Rev. A **48**, 4780 (1993).
[7] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).
[8] J. Ackermann and J. Shertzer, Phys. Rev. A **54**, 365 (1996).
[9] H. Cox, S. J. Smith, and B. T. Sutcliffe, Phys. Rev. A **49**, 4533 (1994); Mol. Phys. **87**, 399 (1996).
[10] A. Kono and S. Hattori, Phys. Rev. A **34**, 1727 (1986).
[11] J. F. Babb and J. Shertzer, Chem. Phys. Lett. **189**, 287 (1992).
[12] D. M. Bishop and L. M. Cheung, Phys. Rev. A **16**, 640 (1977).
[13] The proton mass and all other physical constants used in calculations were chosen from [20].
[14] A. M. Frolov, J. Phys. B **26**, 1031 (1993); Zh. Éksp. Teor. Fiz. **92**, 1959 (1987) [Sov. Phys. JETP **65**, 1100 (1987)].
[15] Request directly from frolova@chem.queensu.ca.
[16] Actually, all δ_i and e_i parameters ($i=1,\ldots,N$) have the optimal values equal zero. Note that it was not assumed initially.
[17] D. P. Chong and D. M. Schrader, Mol. Phys. **16**, 137 (1969).
[18] A. K. Bhatia and R. J. Drachman, Phys. Rev. A **28**, 2523 (1983).
[19] A. M. Frolov and V. H. Smith, Jr., Phys. Rev. A **55**, 2662 (1997).
[20] E. R. Cohen and B. N. Taylor, Phys. Today **45** (8), 9 (1993).
[21] The preliminary evaluations indicate that the proposed two stage procedure will work successfully until the required accuracy is below $\approx 1\times 10^{-20}-10^{-22}$. To produce the higher accuracy the analogous three stage (or even many stage) strategy may be applied.