Three-body hyperspherical method with infinite angular expansions

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The hyperspherical method based on infinite angular expansions is introduced. We approximate the cusp behavior of a wave function using B-spline techniques. Calculations for the ground-state energies of the atomic helium and the e^+Li system are presented as two examples for testing this method. The computed ground-state energy of He is $-2.903\,724$ a.u. with single particle orbitals $l_{\max} = 8$. For the e^+Li system, with $l_{\max} = 9$, the ground-state energy is $-0.250\,83$ a.u., which is better than the configuration interaction result of $-0.250\,107\,82$ a.u. with $l_{\max} = 30$.

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I. INTRODUCTION

Configuration interaction (CI) is one of the most popular methods in atomic structure calculations for systems involving several electrons. In CI the electron-electron potential is expanded as

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^{\infty} \frac{4\pi}{2\lambda+1} \frac{r_<^\lambda}{r_>^{\lambda+1}} \sum_{m=-\lambda}^{\lambda} Y^*_{\lambda m}(\hat{\mathbf{r}}_1) Y_{\lambda m}(\hat{\mathbf{r}}_2), \tag{1}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. The above expansion indicates that many partial waves are needed to achieve an accurate result, which makes radial and angular calculations converge very slowly.

To improve the rate of convergence of CI, Goldman introduced the modified CI (MCI) method which has two major changes to the standard CI: (1) building $r_>$ and $r_<$ in a basis set to represent the cusp behavior of the wave function and (2) mixing a large number of spherical configurations through optimizing a set of nonlinear variational parameters [1,2]. As a result, a better convergence has been obtained over CI. The main problem with MCI is that when the number of angular functions is very large, such as around 300, it becomes difficult to maintain numerical accuracy. This problem was overcome by using the infinite angular expansion method (IAE), in which a vast simplification is introduced using nonlinear functions in the angular basis [3].

On the other hand, the hyperspherical method is an efficient way to study strongly correlated few-body systems. It has been used successfully in atomic and molecular three-body systems [4–8]. However, the application of the hyperspherical method to four-body systems has not yet reached the level of accuracy compared to three-body systems because the hyperspherical method in a body-fixed frame is complicated and cannot be easily extended to a four-body system. The hyperspherical approach in a laboratory frame, however, can be applied to four-body systems directly with angular basis sets expanded using CI. There is, therefore, an important issue of how to improve angular convergence if one wants to extend the hyperspherical method to a four-body system.

In this Brief Report, we apply the IAE-based hyperspherical method to calculate the ground state energies of He and e^+Li. Our intention is to show the efficiency of the present approach applied to three-body systems and the possibility of extension to four-body systems.

II. FORMULATION

In hyperspherical coordinates, the distances of two electrons from the nucleus, r_1 and r_2, are replaced by the hyperradius $R = \sqrt{r_1^2 + r_2^2}$ and the hyperangle $\alpha = \arctan(r_2/r_1)$. The angle α together with the usual polar coordinates (θ_1, ϕ_1) and (θ_2, ϕ_2) of the two electrons are represented collectively as $\Omega = (\alpha, \theta_1, \phi_1, \theta_2, \phi_2)$. The Schrödinger equation is as follows [9]

$$\left(-\frac{1}{2\mu}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + H_{ad}(R,\Omega) - R^2 E\right) \times \psi(R,\Omega) R^{-\frac{3}{2}} (\sin\alpha\cos\alpha)^{-1} = 0\,, \tag{2}$$

where

$$H_{ad}(R,\Omega) = \left(\frac{\Lambda^2 - \frac{1}{4}}{2} + R^2 V(R,\Omega)\right), \tag{3}$$

and

$$\Lambda^2 = -\frac{\partial^2}{\partial\alpha^2} + \frac{\hat{l}_1^2}{\cos^2\alpha} + \frac{\hat{l}_2^2}{\sin^2\alpha}. \tag{4}$$

$V(R,\Omega)$ is the potential of the system.

The adiabatic potentials $U_\nu(R)$ and the corresponding channel function $\Phi_\nu(R,\Omega)$ at the fixed R are obtained by solving the following eigenvalue equation

$$H_{ad}(R,\Omega)\Phi_\nu(R,\Omega) = U_\nu(R)\Phi_\nu(R,\Omega)\,. \tag{5}$$

In this Brief Report, we use B-spline basis functions to expand the channel function

$$\Phi_\nu(R,\Omega) = \sum_{i=1}^{N_\alpha}\sum_{j=1}^{l_{\max}} c_{i,j}^\nu B_{i,k}(\alpha) F_j(\Omega), \tag{6}$$

where $B_{i,k}(\alpha)$ are B-spline functions and k denotes the order of B splines. We choose the following angular functions, as proposed by Goldman and Glickman [3],

$$F_j(\Omega) = \Lambda^{LM}_{l_{1j}l_{2j}}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) e^{\gamma_j \cos\theta_{12}}, \tag{7}$$

TABLE I. Radial convergence for the ground state of helium using the present method and comparisons with other results.

N_α	$N_{\rm DVR}$	N_c	E (a.u.)
40	30	20	−2.879 028 767 296 9
40	40	30	−2.879 028 767 308 5
40	50	30	−2.879 028 767 313 1
40	50	40	−2.879 028 767 314 2
Natural orbital CI [13]			−2.879 026 4
CI with splines [12]			−2.879 028 767 29
Radially uncoupled CI [14]			−2.879 028 767 319 214 408 538

where $\Lambda^{LM}_{l_1 j l_{2j}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ is

$$\Lambda^{LM}_{l_1 j l_{2j}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) = \sum_{m_1 m_2} \langle l_{1j} m_1 l_{2j} m_2 \mid LM\rangle Y_{l_{1j},m_1}(\hat{\mathbf{r}}_1) Y_{l_{2j},m_2}(\hat{\mathbf{r}}_2). \tag{8}$$

The function $e^{\gamma_j \cos\theta_{12}}$ can be expanded in the form

$$e^{\gamma_j \cos\theta_{12}} = \sum_{l=0}^{\infty} (2l+1) u_l(\gamma_j) P_l(\cos\theta_{12}), \tag{9}$$

with the normalized coefficient

$$w_l(\gamma) = \frac{1}{[u_0(2\gamma)]^{1/2}} (2l+1) u_l(\gamma). \tag{10}$$

$P_l(\cos\theta_{12})$ is the Legendre polynomial and $u_l(\gamma_j)$ is the modified spherical Bessel function of the first kind

$$u_l(z) = \left(\frac{\pi}{2z}\right)^{\frac{1}{2}} I_{l+\frac{1}{2}}(z) = (-i)^l j_l(iz). \tag{11}$$

The use of $e^{\gamma_j \cos\theta_{12}}$, which satisfies specific expansion and associative conditions [3], will enhance angular convergence. The angular matrix elements can be evaluated analytically using the orthonormality of $\Lambda^{LM}_{l_1 j l_{2j}}$ and the relation

$$P_l(\cos\theta_{12}) \Lambda^{LM}_{l_1 j l_{2j}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) = \sum_{k_1 k_2} b^L_{l_j k;l} \Lambda^{LM}_{k_1 k_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2), \tag{12}$$

where $b^L_{l_j k;l} = b^L_{l_1 j l_2 j k_1 k_2, l}$, and the form of it can be found in Ref. [3]. The matrix elements of the single-particle angular momentum operator $\hat{l}^2_n$ $(n = 1,2)$ between two basis members $F_{j'}$ and F_j, can be reduced to

$$\begin{aligned}
&\langle F_{j'} | \hat{l}^2_n \mid F_j \rangle \\
&= \sum_q (2q+1) u_q(\gamma) \Big\{ l_{nj}(l_{nj}+1)\big(b^L_{l_j l_{j'};q} - \gamma_j b^L_{l_j l_{j'};1q}\big) \\
&\quad + \gamma_j \sum_{k_1,k_2} k_n(k_n+1) b^L_{l_{j'} k;1} b^L_{l_j k;q} \\
&\quad + \frac{2}{3}\gamma_j^2 \big(b^L_{l_j l_{j'};2q} - b^L_{l_j l_{j'};q}\big) \Big\}.
\end{aligned} \tag{13}$$

We mention that there is a misprint in Eq. (13) in Ref. [3]. The term $\gamma_j \sum_{k_1,k_2} k_n(k_n+1) b^L_{l_{j'} k;1} b^L_{l_j k;q}$ should have a plus sign.

The solution $\psi(R,\Omega)$ of Eq. (2) can be expanded in terms of point-wise discrete variable representation (DVR) basis functions $\pi_j(R)$

$$\psi(R,\Omega) = \sum_{j=1}^{N_{\rm DVR}} \sum_{\mu=1}^{N_c} c_{j\mu} \pi_j(R) \Phi_\mu(R_j,\Omega), \tag{14}$$

where $N_{\rm DVR}$ is the number of terms in the DVR basis set and N_c is the number of coupled channels. Equation (2) can be solved using the slow variable discretization (SVD) method [10].

III. RESULTS AND DISCUSSIONS

The atomic helium is a benchmark system for testing our method. Due to the Pauli exclusion principle, for the ^1S state, the space part of the wave function must be symmetric with respect to the exchange of two electrons. In hyperspherical coordinates this can be satisfied by reducing the interval of α from $0 \leqslant \alpha \leqslant \frac{\pi}{2}$ to $0 \leqslant \alpha \leqslant \frac{\pi}{4}$ with proper boundary conditions. Because of the singularities of the electron-electron potential [see Eq. (1)], the basis sets need to include the cusp behavior of a wave function [11]. In the present method, the cusp behavior can be described handily by adopting k coincident knots at $\alpha = \frac{\pi}{4}$. As a result, the radial convergence can be improved dramatically, which can be tested by keeping only the terms with $\lambda = 0$ in the expansion of r_{12}^{-1}. The results are shown in Table I. From the table, we can see that the present result is converged to 10^{-11} in double precision arithmetic. Decleva *et al.* [12] also performed the radial convergence test using B-spline basis sets but with no special treatment on the singularities. Their result is found to be accurate to 10^{-8}. We can see that our method can deal with radial correlations more efficiently. With $N_\alpha = 60$, $l_{\rm max} = 8$ ($l_{\rm max}$ is the number of the partial wave), $N_c = 20$, and $N_{\rm DVR} = 60$, using our approach the ground-state energy of He can be calculated to −2.903 724 21, which is close to the value of −2.903 724 287 given by the authors of Ref. [2]. Thus, the present method could work well for ordinary three-body systems.

Next we consider the e^+-Li system, a two-center problem, which is more difficult to deal with than ordinary three-body systems. In this system, the electron-positron correlations are so strong that they are coalescing into a Ps cluster. The accurate representation of the Ps cluster by single-particle functions requires the inclusion of high angular momentum quantum numbers. As noted by Bromley *et al.* [15], they used $l_{\rm max} = 30$ to obtain a definite evidence of forming a bound state for e^+Li in their CI calculations. Thus, the present method may be considered to be more efficient if it could be applied to

TABLE II. Comparisons of the calculated bound state energies of Li to the experiment values and other results. All values are in atomic units.

	Present	Bromley [15]	Experiment [17]
$2s$	−0.197 952	−198 115 0	−0.198 14
$2p$	−0.130 218	−0.130 015 2	−0.130 24
$3s$	−0.074 224	−0.074 162 2	−0.074 18
$3p$	−0.057 242	−0.057 156 0	−0.057 24
$3d$	−0.055 615	−0.055 611 8	−0.055 61
$4d$	−0.031 279	−0.031 264 2	−0.031 27

the e^+-Li system. We attempt to improve convergence in two directions: the angular correlations as included in the IAE method and the radial correlations as represented by optimizing the knot distribution of B splines. The guiding principle of distributing knots is to put more knots near the particle-particle coalescence points and use $k-2$ coincident knots at $\alpha = \frac{\pi}{4}$ so that the radial cusp behavior of the wave function can be sufficiently described. The e^+-Li system is treated as an effective three-body system consisting of a core, an electron, and a positron. The core is assumed to have infinite mass. We adopt the model potential given by Peach *et al.* [16] to describe the interaction between the core and electron. Using this model potential, we have calculated the energies of the ground and excited states of Li by diagonalizing the Hamiltonian using B-spline basis functions. The calculated energies are nicely comparable with the experimental results, as shown in Table II.

Table III shows the angular convergence of the ground-state energy of e^+Li obtained in this work and the CI calculations [15]. Basis sets with $N_\alpha = 130$, $N_c = 15$, and $N_{\rm DVR} = 60$ are used in our calculations. We have made an extensive convergence study for the ground-state energy with respect to the basis sets and we ensured that the ground-state energy has converged to four significant figures. From the table, we can see that our results converge faster than those obtained by CI. With only $l_{\max} = 9$ generalized angular functions, the calculated energy is −0.250 83 which is lower than −0.250 107 82 obtained using CI [15] with $l_{\max} = 30$. The large difference is mainly due to different methods used because the influence caused by the model potentials is small. From Table II, we can see that the bound-state energies of Li obtained by using different model potentials are close to each other. Table III also lists two CI-type calculations, where CI(14) is the result obtained by Bromley *et al.* [18] using the CI method with single particle orbitals $l_{\max} = 14$ and CI-HY is the result obtained by Clary [19] using the CI plus Hylleraas approach. Note that these two CI-type approaches fail to predict the existence of bound states in e^+Li. We also list the results by the finite element method (FEM), the hyperspherical method, and the fixed core stochastic variational method (FCSVM) [20–23]. Though the present results have not converged to the value given by the non-CI methods, in the framework of CI calculations, we can see that the efficiency of the present method is superior to that of the standard CI.

TABLE III. Comparison of the ground-state energy of e^+Li and angular convergence obtained in this work and from the CI calculations [15]. $l_{\max}$ refers to the largest angular momentum used. All values are in atomic units.

$l_{\max}$	Present	CI [15]
9	−0.250 83	−0.241 605 76
10	−0.251 02	−0.243 023 09
11	−0.251 70	
12	−0.251 73	−0.245 116 08
13	−0.251 99	
15	−0.252 16(24)	−0.247 561 64
30		−0.250 107 82
CI(14) [18]	−0.242 087 11	
CI-HY [19]	−0.229 499	
FEM [22]	−0.252 37(10)	
Hyper [23]	−0.252 447	
FCSVM [20,21]	−0.252 477	

The normalized coefficient in the expansion of Eq. (9) will give the relative distribution of different values of l. This distribution is presented in Fig. 1, where each curve corresponds to one value of γ. The mixing of different angular orbitals is clearly seen. The larger the value of γ, the larger the value of l is mixed. Notice that with 15 generalized angular functions, at least 80 angular functions are mixed.

The extension of the present method to atomic four-body systems, such as e^+He, is straightforward. In contrast to the proposal seen in Ref. [3], we suggest that the angular functions should be written as follows

$$F_j(1,2;3) = \Lambda^{K_{12}LM}_{l_{1j}l_{2j}l_{3j}}(1,2;3) \times (e^{\gamma_{1j}\cos\theta_{12}} + e^{\gamma_{2j}\cos\theta_{23}} + e^{\gamma_{3j}\cos\theta_{31}}), \quad (15)$$

where $\Lambda^{K_{12}LM}_{l_{1j}l_{2j}l_{3j}}(1,2;3)$ has the following form:

$$\Lambda^{K_{12}LM}_{l_{1j}l_{2j}l_{3j}}(1,2;3) = \sum_{M_{12},m_{3j}} \langle K_{12}M_{12}l_{3j}m_{3j} \mid LM\rangle \Lambda^{K_{12}M_{12}}_{l_{1j}l_{2j}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) Y_{l_{3j}m_{3j}}(\hat{\mathbf{r}}_3). \quad (16)$$

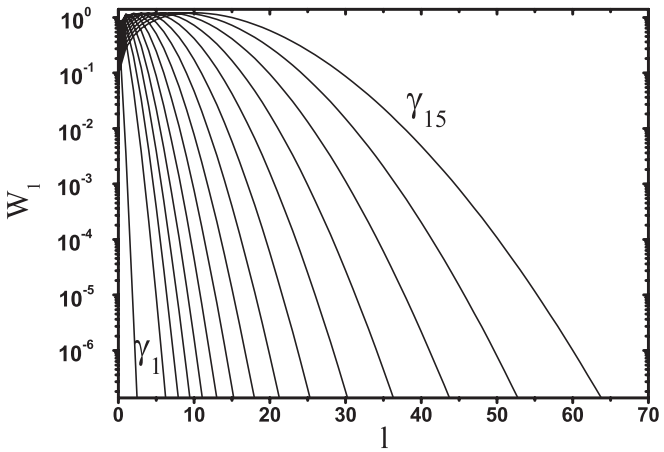

FIG. 1. Relative distribution of single-orbital angular functions for a basis set with 15 exponential-type generalized angular functions. l refers to the quantum number of $P_l(\cos\theta_{12})$, and w_l is the normalized coefficient in the expansion of $e^{\gamma\cos\theta_{12}}$.

Using the recoupling transformations

$$\Lambda^{K_{12}LM}_{l_{1j}l_{2j}l_{3j}}(1,2;3) = \sum_{K_{23}} \Lambda^{K_{23}LM}_{l_{1j}l_{2j}l_{3j}}(2,3;1)(-1)^{l_{1j}+l_{2j}+l_{3j}+L} \times [K_{12},K_{23}]^{1/2} \begin{Bmatrix} l_{1j} & l_{2j} & K_{12} \\ l_{3j} & L & K_{23} \end{Bmatrix}, \quad (17)$$

$$\Lambda^{K_{12}LM}_{l_{1j}l_{2j}l_{3j}}(1,2;3) = \sum_{K_{13}} \Lambda^{K_{13}LM}_{l_{1j}l_{3j}l_{2j}}(1,3;2)(-1)^{l_{1j}+l_{2j}+l_{3j}+L} \times [K_{12},K_{13}]^{1/2} \begin{Bmatrix} l_{2j} & l_{1j} & K_{12} \\ l_{3j} & L & K_{13} \end{Bmatrix}, \quad (18)$$

and Eq. (12), closed-form expressions for angular matrix elements can also be found easily.

IV. CONCLUSION

In conclusion, we have described the hyperspherical method based on the infinite angular expansions. We have approximated the cusp behavior of a wave function using B-spline techniques. Calculations of the ground-state energies for He and e^+Li have been performed as examples to test the method. The calculated ground-state energy of He is $-2.903\,724$ a.u. with single particle orbitals $l_{\max} = 8$. For e^+Li, the ground-state energy is $-0.250\,83$ a.u. with $l_{\max} = 9$, which is better than the CI calculation of $-0.250\,107\,82$ a.u. with $l_{\max} = 30$. It can be seen that the present method is superior to that of standard CI. We have also discussed the extension of the present method to systems involving more than two electrons and suggest a new combination mode of angular functions.

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