Theor Chem Acc (1997) 98:110–116

Theoretical
Chemistry Accounts

A potential harmonic method for the three-body coulomb problem

Wensheng Bian, Conghao Deng

Institute of Theoretical Chemistry, Shandong University, Jinan, 250100, People's Republic of China

Received: 5 September 1996 / Accepted: 14 July 1997

Abstract. A potential harmonic method that is suitable for the three-body coulomb systems is presented. This method is applied to solve the three-body Schroedinger equations for He and $e^+e^-e^+$ directly, and the calculations yield very good results for the energy. For example, we obtain a ground-state energy of -0.26181 hartrees for $e^+e^-e^+$, and -2.90300 hartrees for He with finite nuclear mass, in good agreement with the exact values of -0.26200 hartrees and -2.90330 hartrees. Compared with the full-set calculations, the errors in the total energy for ground and excited states of $e^+e^-e^+$ are very small, around -0.0001 hartrees. We conclude that the present method is one of the best PH methods for the three-body coulomb problem.

Key words: Three-body problem – Schroedinger equation – Potential harmonics – Hyperspherical coordinate – Generalized Laguerre function

1 Introduction

The potential harmonics (PHs) are those hyperspherical harmonics (HHs) that appear in the expansion of the product of the potential and the dominant term occurring in the expansion of the wavefunction. Fabre de la Ripelle [1, 2, and the references therein] found that these harmonics (or PHs) are the ones which contribute most importantly to the wavefunction, and in some test cases there is only a small loss in accuracy by using the PH basis instead of the full HH basis. PHs are specific linear combinations of HHs with the same global angular momentum (K). In the simplest case, only one PH is obtained for each value of K, and the degeneracy of HHs at large K is very high; thus the PH method is very efficient in reducing the number of HHs used in the expansion. This removes one of the main impediments that has seriously hindered the HH technique from further applications [1–4].

Correspondence to: W. Bian

Several years ago, Fabre de la Ripelle et al. [4] proposed a PH method which was believed to be able to include e-e correlations into the basis effectively, and showed that this PH method was the most accurate and gave the best results in their test cases involving helium and H^-. However, when they introduced their method, Fabre de la Ripelle et al. [4] used a mathematical formalism which was only suitable for two-electron atomic systems, such as helium and H^- where the mass of the nucleus was treated as infinite.

The main purpose of the present paper is to establish a PH method that is suitable for the general three-body coulomb systems and at the same time, can match the performance of the new PH method of Fabre de la Ripelle et al. [4] in the particular case of He(H^-). In our method, two sets of orthonormal PH basis functions are constructed and used in the expansion of the wavefunction; analytic expressions for matrix elements with these PH functions are derived. Finally the generalized Laguerre function (GLF) expansion method, which was recently developed by Deng and others [5–8], is used in the solution of the coupled differential equations. Programs based on this method have been successfully implemented and the calculations for He atom and positronium ion $e^+e^-e^+$ have yielded very good results for the energy.

A detailed presentation of our method is given in the next section, and the practical calculations are reported in Sect. 3.

2 Theoretical method

2.1 Solution of the Schroedinger equation

The nonrelativistic Schroedinger equation for the general three-body coulomb problem can be written as

$$\left(-\sum_{i=1}^{3}\frac{\nabla_i^2}{2m_i}+V-E\right)\Psi=0\ , \tag{1}$$

where V is the coulomb potential and m_i is the mass of particle i. Consider a system with two identical particles; in particles we assume that particles 1 and 2 are identical, and $m_1=m_2=m$.

In the center-of-mass system, Eq. (1) has the form [9, 10]

$$[-\tfrac{1}{2}(\nabla_{\xi}^2+\nabla_{\xi'}^2)+V-E]\Psi=0 \ , \tag{2}$$

$$\xi=\frac{1}{\sqrt{2}}(\mathbf{r}_1-\mathbf{r}_2)$$

$$\xi'=\sqrt{\frac{M}{2(M+2)}}(\mathbf{r}_1+\mathbf{r}_2-2\mathbf{r}_3) \ , \tag{3}$$

where we used the units $m=\hbar=e=1$; M is the mass of the unidentical particle; $\mathbf{r}_i$ is the position vector of the particle i; ξ and ξ' are relative coordinate vectors.

For the S state ($L=0$), ξ and ξ' can be expressed in terms of hyperspherical coordinates by the relations

$$\xi_1=-\rho\cos\left(\frac{\pi}{4}-\frac{a}{2}\right)\cos\frac{\lambda}{2}$$

$$\xi_2=\rho\sin\left(\frac{\pi}{4}-\frac{a}{2}\right)\sin\frac{\lambda}{2}$$

$$\xi_3=0$$

$$\xi_1'=-\rho\cos\left(\frac{\pi}{4}-\frac{a}{2}\right)\sin\frac{\lambda}{2}$$

$$\xi_2'=-\rho\sin\left(\frac{\pi}{4}-\frac{a}{2}\right)\cos\frac{\lambda}{2}$$

$$\xi_3'=0 \ , \tag{4}$$

where $\rho(0\le\rho<\infty)$ is the hyperradial variable; $a(0\le a<\frac{\pi}{2})$, and $\lambda(0\le\lambda<2\pi)$ are two hyper-angles.

In these hyperspherical variables, Eq. (2) takes the form

$$\left[\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2}+\frac{5}{\rho}\frac{\partial}{\partial\rho}-\frac{\Lambda^2}{\rho^2}\right)+\frac{Z(\Omega)}{\rho}+E\right]\Psi=0 \ , \tag{5}$$

where $V=-\frac{Z(\Omega)}{\rho}$, Ω stands for the hyperangular variables a, and λ; Λ^2 is the generalized scalar angular-momentum operator and for $L=0$,

$$\Lambda^2=-4\left(\frac{\partial^2}{\partial a^2}+2\cot 2a\frac{\partial}{\partial a}+\frac{1}{\sin^2 a}\frac{\partial^2}{\partial\lambda^2}\right) \ . \tag{6}$$

Now we expand Ψ in terms of two sets of PH basis functions, which are denoted by $Y_{\mu}^{A}(\lambda, a)$ and $Y_{\mu'}^{B}(\lambda, a)$ (the definitions and derivations about them are given in Sect. 2.2):

$$\Psi=\sum_{\mu}\Theta_{\mu}^{A}(\rho)Y_{\mu}^{A}(\lambda, a)+\sum_{\mu'}\Theta_{\mu'}^{B}(\rho)Y_{\mu'}^{B}(\lambda, a) \ . \tag{7}$$

The number of PH functions for the first set is denoted as N_1, and that for the second set is denoted as N_2. We assume N is the total number of PH functions; then $N=N_1+N_2$. $Y_{\mu}(\lambda, a)$ are solutions (for the S states) of the equation:

$$\begin{aligned}\Lambda^2 Y_{\mu}(\lambda, a)&=2\mu(2\mu+4)Y_{\mu}(\lambda, a)(\mu=0, 1, 2, \cdots)\\&=K(K+4)Y_{\mu}(\lambda, a)(K=2\mu)\end{aligned} \tag{8}$$

and thus can be expressed in terms of the usual Wigner D functions ($D_{mm'}^{l}(\alpha, \beta, \gamma)$). Equation (7) can be written in the matrix form:

$$\Psi=\mathbf{Y}^{A}\mathbf{\Theta}^{A}+\mathbf{Y}^{B}\mathbf{\Theta}^{B} \ , \tag{9}$$

where $\mathbf{Y}^{A}$ and $\mathbf{Y}^{B}$ are N_1- and N_2-dimensional line matrices respectively, whereas $\mathbf{\Theta}^{A}$ and $\mathbf{\Theta}^{B}$ are N_1- and N_2-dimensional column matrices respectively. We further let

$$\mathbf{Y}=(\mathbf{Y}^{A}, \mathbf{Y}^{B}) \tag{10}$$

and

$$\mathbf{\Theta}=\begin{pmatrix}\mathbf{\Theta}^{A}\\ \mathbf{\Theta}^{B}\end{pmatrix} \ . \tag{11}$$

Then Eq. (9) can be rewritten as:

$$\Psi=\mathbf{Y}\mathbf{\Theta} \ , \tag{12}$$

where $\mathbf{Y}$ is the N-dimensional line matrix, and $\mathbf{\Theta}$ is the N-dimensional column matrix.

After substituting Eq. (12) into Eq. (5) and integrating out the hyperangular part of the wavefunction, we can obtain a matrix equation:

$$\left[\frac{d^2}{d\rho^2}+\frac{5}{\rho}\frac{d}{d\rho}-\frac{\mathbf{K}(\mathbf{K}+4)}{\rho^2}+2\frac{\mathbf{Z}}{\rho}+2E\right]\mathbf{\Theta}=0 \ , \tag{13}$$

where $\mathbf{K}$ is $N\times N$ diagonal matrix, with the diagonal elements being 2μ for the preceding N_1 elements and $2\mu'$ for the following N_2 elements; N is the number of PHs used (as mentioned above); $\mathbf{Z}$ is $N\times N$ matrix,

$$\mathbf{Z}=\begin{pmatrix}\mathbf{Z}_{AA} & \mathbf{Z}_{AB}\\ \mathbf{Z}_{BA} & \mathbf{Z}_{BB}\end{pmatrix} \ . \tag{14}$$

The matrix elements for $\mathbf{Z}_{AA}$, $\mathbf{Z}_{AB}$, $\mathbf{Z}_{BA}$, $\mathbf{Z}_{BB}$ are the following angular integration respectively:

$$\mathbf{Z}_{A\mu A\mu'}=\langle Y_{\mu}^{A}|Z(\Omega)|Y_{\mu'}^{A}\rangle \ , \tag{15}$$

$$\mathbf{Z}_{B\mu B\mu'}=\langle Y_{\mu}^{B}|Z(\Omega)|Y_{\mu'}^{B}\rangle \ , \tag{16}$$

$$\mathbf{Z}_{A\mu B\mu'}=\langle Y_{\mu}^{A}|Z(\Omega)|Y_{\mu'}^{B}\rangle \ , \tag{17}$$

$$\mathbf{Z}_{B\mu A\mu'}=\langle Y_{\mu}^{B}|Z(\Omega)|Y_{\mu'}^{A}\rangle \ , \tag{18}$$

and the analytic expressions for them are derived out in Sect. 2.3. Now we let

$$\mathbf{\Theta}=e^{-\beta\rho}\mathbf{\Phi} \tag{19}$$

and

$$\beta^2=-2E \ . \tag{20}$$

Substitution of Eq. (19) into Eq. (13) yields

$$\left[\frac{d^2}{d\rho^2}+\left(\frac{5}{\rho}-2\beta\right)\frac{d}{d\rho}-\frac{\mathbf{K}(\mathbf{K}+4)}{\rho^2}+\frac{2\mathbf{Z}-5\beta}{\rho}\right]\mathbf{\Phi}=0 \ . \tag{21}$$

We define

$$R=2\beta\rho \ . \tag{22}$$

Then we have

$$\left[\frac{d^2}{dR^2}+\left(\frac{5}{R}-1\right)\frac{d}{dR}-\frac{\mathbf{K}(\mathbf{K}+4)}{R^2}+\frac{\frac{\mathbf{Z}}{\beta}-\frac{5}{2}}{R}\right]\mathbf{\Phi}=0 \ . \tag{23}$$

We expand $\mathbf{\Phi}(R)$ in terms of generalized Laguerre functions (GLF) [5, 6]

$$\mathbf{\Phi}(R) = \sum_{n=0}^{\infty} \boldsymbol{C_n} L_n^{\alpha}(R) \text{ (we choose } \alpha = 4) \ , \tag{24}$$

where $\mathbf{C}_n$ is the column matrix of expansion coefficients, and $L_n^{\alpha}(R)$ is the generalized Laguerre function.

By using the following properties of the GLF,

$$\left[\frac{d^2}{dR^2} + \left(\frac{5}{R} - 1\right)\frac{d}{dR} + \frac{n}{R}\right] L_n^4(R) = 0$$

$$RL_n^4 = -(n+4)L_{n-1}^4 + (2n+5)L_n^4 - (n+1)L_{n+1}^4 \ , \tag{25}$$

we can finally get the recurrence relation of the expansion coefficients:

$$\mathbf{a}(C_n)\mathbf{C}_n + \mathbf{a}(C_{n+1})\mathbf{C}_{n+1} + \mathbf{a}(C_{n-1})\mathbf{C}_{n-1} = 0 \tag{26}$$

where

$$\mathbf{a}(C_n) = \mathbf{K}(\mathbf{K}+4) - (2n+5)\left(\frac{\mathbf{Z}}{\beta} - n - \frac{5}{2}\right)$$

$$\mathbf{a}(C_{n+1}) = (n+5)\left(\frac{\mathbf{Z}}{\beta} - n - \frac{7}{2}\right)$$

$$\mathbf{a}(C_{n-1}) = n\left(\frac{\mathbf{Z}}{\beta} - n - \frac{3}{2}\right) \ . \tag{27}$$

From Eq. (26), a generalized eigenvalue equation about β can be easily obtained,

$$\mathbf{AC} = \beta \mathbf{BC} \ , \tag{28}$$

in which

$$\mathbf{A}_{n,n} = -(2n+5)\mathbf{Z}$$

$$\mathbf{A}_{n,n+1} = (n+5)\mathbf{Z}$$

$$\mathbf{A}_{n,n-1} = n\mathbf{Z} \ , \tag{29}$$

$$\mathbf{B}_{n,n} = -\mathbf{K}(\mathbf{K}+4) - (2n+5)\left(n + \frac{5}{2}\right)$$

$$\mathbf{B}_{n,n+1} = (n+5)\left(n + \frac{7}{2}\right)$$

$$\mathbf{B}_{n,n-1} = n\left(n + \frac{3}{2}\right) \ , \tag{30}$$

($n = 0, 1, \cdots$, and the other elements of $\mathbf{A}$ and $\mathbf{B}$ are zero), and $\mathbf{C}$ is a M-dimensional column matrix; $\mathbf{A}$, $\mathbf{B}$ are $M \times M$ square matrices; $M = N$ (the number of PHs) $\times$ *NGLF* (the number of GLF). Equation (28) is solved numerically and thereby the wavefunction and the energy eigenvalue are obtained.

2.2 PH basis sets

The two sets of PH basis functions, Y_{μ}^{A} and $Y_{\mu'}^{B}$ [or $Y_{\mu}^{A}(\lambda, a)$ and $Y_{\mu'}^{B}(\lambda, a)$], used in the expansion of the wavefunction in Eq. (7) are obtained in the following way.

The interaction potential for the three-body coulomb systems considered in this paper is written as

$$V = -\frac{Z(\Omega)}{\rho} = -\frac{z}{r_{13}} - \frac{z}{r_{23}} + \frac{1}{r_{12}} \ . \tag{31}$$

Here, z is the nuclear charge and r_{ij} is the distance between particles, which can be expressed with the hyperspherical coordinates [10]:

$$r_{ij} = \rho\sqrt{k_{ij}(1 + \sin a\cos(\lambda + \omega_{ij}))} \ , \tag{32}$$

where $k_{ij} = 1, \frac{M+1}{2M}, \frac{M+1}{2M}$ and $\omega_{ij} = 0, \omega, -\omega$ with $\omega = \arccos\frac{-1}{M+1}$, for $ij = 12, 23, 13$ respectively.

Based on Eq.(32), the following expansion formula can be obtained [10]:

$$\frac{1}{r_{ij}} = \frac{16}{\rho\pi\sqrt{2\kappa_{ij}}} \sum_{\mu=0}^{\infty} \frac{(-1)^{\mu}(\mu+1)}{(2\mu+3)(2\mu+1)} \sum_{v=-\mu}^{\mu} (-1)^{\frac{\mu-v}{2}} \exp(-i\omega_{ij}v) D^{\frac{\mu}{2}}_{\frac{v}{2}-\frac{v}{2}}(2\lambda, 2a, 0) \ , \tag{33}$$

where $D^{l}_{mm'}(\alpha, \beta, \gamma)$ are usual Wigner D functions.

From Eq. (33), we define the PH function for the interparticle potential $\frac{1}{r_{ij}}$ as

$$Y'_{\mu}(ij) = \sum_{v=-\mu}^{\mu} (-1)^{\frac{\mu-v}{2}} \exp(-i\omega_{ij}v) D^{\frac{\mu}{2}}_{\frac{v}{2}-\frac{v}{2}}(2\lambda, 2a, 0) \ . \tag{34}$$

Then

$$\frac{1}{r_{ij}} = \frac{16}{\rho\pi\sqrt{2\kappa_{ij}}} \sum_{\mu=0}^{\infty} \frac{(-1)^{\mu}(\mu+1)}{(2\mu+3)(2\mu+1)} Y'_{\mu}(ij) \ . \tag{35}$$

The Pauli exclusion principle requires that the wavefunction be antisymmetric under interchange of the two identical particles, and thus we can obtain two sets of PH functions for the ^1S state from Eq. (34), which satisfy the Pauli principle:

$$Y'^{a}_{\mu} = Y'_{\mu}(12) \ , \tag{36}$$

$$Y'^{b}_{\mu} = Y'_{\mu}(13 + 23) \ . \tag{37}$$

Here we let

$$Y'_{\mu}(13 + 23) = Y'_{\mu}(13) + Y'_{\mu}(23) \ . \tag{38}$$

By using Eq. (34) we can further obtain

$$Y'_{\mu}(12) = \sum_{v=-\mu}^{\mu} (-1)^{\frac{\mu-v}{2}} D^{\frac{\mu}{2}}_{\frac{v}{2}-\frac{v}{2}}(2\lambda, 2a, 0) \ , \tag{39}$$

$$Y'_{\mu}(13 + 23) = \sum_{v=-\mu}^{\mu} (-1)^{\frac{\mu-v}{2}} 2\cos\omega v D^{\frac{\mu}{2}}_{\frac{v}{2}-\frac{v}{2}}(2\lambda, 2a, 0) \ . \tag{40}$$

On the basis of Eq. (36) and Eq. (37), we have constructed another two sets of PH bases, which are orthogonal to each other, by the method of Gram-Schmidt:

$$Y'^{A}_{\mu} = Y'_{\mu}(12) \ , \tag{41}$$

$$Y'^{B}_{\mu} = a_{\mu} Y'_{\mu}(12) + Y'_{\mu}(13 + 23)$$

($\mu \neq 0,1$ and for the particular case $M = \infty, \mu \neq 0, \text{odd}$) (42)

with

$$a_\mu = -\frac{2C_\mu^1(\cos\omega)}{\mu+1} \quad , \tag{43}$$

where $C_\mu^1(\cos\omega)$ is the Gegenbauer polynomial. $Y_\mu'^A$ and $Y_\mu'^B$ can be easily normalized by the angular integration procedure and finally we obtain the two sets of orthonormal PH bases:

$$Y_\mu^A = \pi^{-\frac{3}{2}} Y_\mu'^A \quad , \tag{44}$$

$$Y_\mu^B = \frac{Y_\mu'^B}{N_\mu^B} \tag{45}$$

with

$$(N_\mu^B)^2 = 2\pi^3 \left\{ 1 + \frac{C_\mu^1(\cos 2\omega)}{\mu+1} - 2\left[\frac{C_\mu^1(\cos\omega)}{\mu+1}\right]^2 \right\} \quad . \tag{46}$$

2.3 Analytic expressions for Z-matrix elements

Firstly, let us consider some angular integration fromula with three PH basis functions. Let

$$I_1(\mu,\mu',\mu'') = \left\langle Y_\mu'(13+23) \middle| Y_{\mu''}'(13+23) \middle| Y_{\mu'}'(13+23) \right\rangle \quad , \tag{47}$$

with the integration being taken over

$$d\Omega = \frac{\pi^2}{4} \sin 2a d\lambda d(2a) \quad . \tag{48}$$

Substitution of Eq. (40) into Eq. (47) leads to

$$I_1(\mu,\mu',\mu'') = \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \sum_{\nu''=-\mu''}^{\mu''} (-1)^{\frac{\mu-\nu+\mu'-\nu'+\mu''-\nu''}{2}} 8\cos\omega\nu\cos\omega\nu'\cos\omega\nu'' \left\langle D^{\frac{\mu}{2}}_{\frac{\nu}{2}-\frac{\nu}{2}} \middle| D^{\frac{\mu''}{2}}_{\frac{\nu''}{2}-\frac{\nu''}{2}} \middle| D^{\frac{\mu'}{2}}_{\frac{\nu'}{2}-\frac{\nu'}{2}} \right\rangle \quad . \tag{49}$$

According to formula [11]

$$D^{\frac{\mu_1}{2}}_{\frac{\nu_1}{2}\frac{\nu_1'}{2}} D^{\frac{\mu_2}{2}}_{\frac{\nu_2}{2}\frac{\nu_2'}{2}} = \sum_{\mu_3=|\mu_1-\mu_2|}^{\mu_1+\mu_2} D^{\frac{\mu_3}{2}}_{\frac{\nu_1+\nu_2}{2}\frac{\nu_1'+\nu_2'}{2}} \left(\frac{\mu_1}{2},\frac{\nu_1}{2},\frac{\mu_2}{2},\frac{\nu_2}{2} \middle| \frac{\mu_3}{2},\frac{\nu_1+\nu_2}{2}\right) \times \left(\frac{\mu_1}{2},\frac{\nu_1'}{2},\frac{\mu_2}{2},\frac{\nu_2'}{2} \middle| \frac{\mu_3}{2},\frac{\nu_1'+\nu_2'}{2}\right) \quad , \tag{50}$$

where the $(l,m,l',m'|l'',m'')$ are the Clebsch-Gordan coefficients of su (2) group, and

$$\left\langle D^{\frac{\mu_1}{2}}_{\frac{\nu_1}{2}\frac{\nu_1'}{2}} \middle| D^{\frac{\mu_2}{2}}_{\frac{\nu_2}{2}\frac{\nu_2'}{2}} \right\rangle = \delta_{\mu_1\mu_2}\delta_{\nu_1\nu_2}\delta_{\nu_1'\nu_2'} \frac{\pi^3}{\mu_1+1} \quad , \tag{51}$$

we have

$$\left\langle D^{\frac{\mu_3}{2}}_{\frac{\nu_3}{2}\frac{\nu_3'}{2}} \middle| D^{\frac{\mu_1}{2}}_{\frac{\nu_1}{2}\frac{\nu_1'}{2}} \middle| D^{\frac{\mu_2}{2}}_{\frac{\nu_2}{2}\frac{\nu_2'}{2}} \right\rangle = \left(\frac{\mu_1}{2},\frac{\nu_1}{2},\frac{\mu_2}{2},\frac{\nu_2}{2} \middle| \frac{\mu_3}{2},\frac{\nu_3}{2}\right) \times \left(\frac{\mu_1}{2},\frac{\nu_1'}{2},\frac{\mu_2}{2},\frac{\nu_2'}{2} \middle| \frac{\mu_3}{2},\frac{\nu_3'}{2}\right) \frac{\pi^3}{\mu_3+1} \quad . \tag{52}$$

Thus, Eq. (49) can be further written as

$$I_1(\mu,\mu',\mu'') = \frac{8\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1} \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \cos\omega\nu\cos\omega\nu'\cos\omega(\nu-\nu') \left(\frac{\mu'}{2},\frac{\nu'}{2},\frac{\mu''}{2},\frac{\nu-\nu'}{2} \middle| \frac{\mu}{2},\frac{\nu}{2}\right)^2 \quad . \tag{53}$$

Similarly we achieve

$$I_2(\mu,\mu',\mu'') = \left\langle Y_\mu'(13+23) \middle| Y_{\mu''}'(12) \middle| Y_{\mu'}'(12) \right\rangle = \frac{2\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1} \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \cos\omega\nu \left(\frac{\mu'}{2},\frac{\nu'}{2},\frac{\mu''}{2},\frac{\nu-\nu'}{2} \middle| \frac{\mu}{2},\frac{\nu}{2}\right)^2 \quad , \tag{54}$$

$$I_3(\mu,\mu',\mu'') = \left\langle Y_\mu'(12) \middle| Y_{\mu''}'(13+23) \middle| Y_{\mu'}'(12) \right\rangle = \frac{2\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1} \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \cos\omega(\nu-\nu') \left(\frac{\mu'}{2},\frac{\nu'}{2},\frac{\mu''}{2},\frac{\nu-\nu'}{2} \middle| \frac{\mu}{2},\frac{\nu}{2}\right)^2 \quad , \tag{55}$$

$$I_4(\mu,\mu',\mu'') = \left\langle Y_\mu'(12) \middle| Y_{\mu'}'(13+23) \middle| Y_{u''}'(12) \right\rangle = \frac{2\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1} \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \cos\omega\nu' \left(\frac{\mu'}{2},\frac{\nu'}{2},\frac{\mu''}{2},\frac{\nu-\nu'}{2} \middle| \frac{\mu}{2},\frac{\nu}{2}\right)^2 \quad , \tag{56}$$

$$I_5(\mu,\mu',\mu'') = \left\langle Y_\mu'(12) \middle| Y_{\mu'}'(13+23) \middle| Y_{u''}'(13+23) \right\rangle = \frac{4\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1} \sum_{\nu=-\mu}^{\mu} \sum_{\nu'=-\mu'}^{\mu'} \cos\omega\nu'\cos\omega(\nu-\nu') \left(\frac{\mu'}{2},\frac{\nu'}{2},\frac{\mu''}{2},\frac{\nu-\nu'}{2} \middle| \frac{\mu}{2},\frac{\nu}{2}\right)^2 \quad , \tag{57}$$

$$I_6(\mu,\mu',\mu'') = \left\langle Y'_{\mu}(13+23)\middle|Y'_{\mu'}(13+23)\middle|Y'_{u''}(12)\right\rangle$$
$$= \frac{4\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1}\sum_{v=-\mu}^{\mu}\sum_{v'=-\mu'}^{\mu'}\cos\omega v\cos\omega v'$$
$$\left(\frac{\mu'}{2},\frac{v'}{2},\frac{\mu''}{2},\frac{v-v'}{2}\middle|\frac{\mu}{2},\frac{v}{2}\right)^2 , \tag{58}$$

$$I_7(\mu,\mu',\mu'') = \left\langle Y'_{\mu}(13+23)\middle|Y'_{\mu'}(12)\middle|Y'_{u''}(13+23)\right\rangle$$
$$= \frac{4\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1}$$
$$\sum_{v=-\mu}^{\mu}\sum_{v'=-\mu'}^{\mu'}\cos\omega v\cos\omega(v-v')$$
$$\left(\frac{\mu'}{2},\frac{v'}{2},\frac{\mu''}{2},\frac{v-v'}{2}\middle|\frac{\mu}{2},\frac{v}{2}\right)^2 , \tag{59}$$

$$I_8(\mu,\mu',\mu'') = \left\langle Y'_{\mu}(12)\middle|Y'_{\mu'}(12)\middle|Y'_{u''}(12)\right\rangle$$
$$= \frac{\pi^3(-1)^{\mu+\mu'+\mu''}}{\mu+1}\sum_{v=-\mu}^{\mu}\sum_{v'=-\mu'}^{\mu'}$$
$$\left(\frac{\mu'}{2},\frac{v'}{2},\frac{\mu''}{2},\frac{v-v'}{2}\middle|\frac{\mu}{2},\frac{v}{2}\right)^2 . \tag{60}$$

Now, let us consider the **Z**-matrix. As mentioned in Sect. 2.1, **Z** is $N\times N$ matrix: $\begin{pmatrix}\mathbf{Z}_{AA} & \mathbf{Z}_{AB}\\ \mathbf{Z}_{BA} & \mathbf{Z}_{BB}\end{pmatrix}$ and the matrix elements for $\mathbf{Z}_{AA}, \mathbf{Z}_{AB}, \mathbf{Z}_{BA}, \mathbf{Z}_{BB}$ are the following angular integrations respectively:

$$\mathbf{Z}_{A\mu A\mu'} = \langle Y^A_{\mu}|Z(\Omega)|Y^A_{\mu'}\rangle , \tag{61}$$

$$\mathbf{Z}_{B\mu B\mu'} = \langle Y^B_{\mu}|Z(\Omega)|Y^B_{\mu'}\rangle , \tag{62}$$

$$\mathbf{Z}_{A\mu B\mu'} = \langle Y^A_{\mu}|Z(\Omega)|Y^B_{\mu'}\rangle , \tag{63}$$

$$\mathbf{Z}_{B\mu A\mu'} = \langle Y^B_{\mu}|Z(\Omega)|Y^A_{\mu'}\rangle . \tag{64}$$

Here, the integration is taken over $d\Omega$ [See Eq. (48)]. From Eq. (31) and Eq. (35), we get

$$Z(\Omega) = \sum_{\mu=0}^{\infty} B_{\mu}\left[a(z,M)Y'_{\mu}(13+23) - \frac{1}{\sqrt{2}}Y'_{\mu}(12)\right] , \tag{65}$$

where

$$B_{\mu} = \frac{16(-1)^{\mu}(\mu+1)}{\pi(2\mu+3)(2\mu+1)} , \tag{66}$$

$$a(z,M) = z\sqrt{\frac{M}{M+1}} . \tag{67}$$

Based on the integration formula in Eqs. (53)–(60), the explicit expressions for Eqs. (61)–(64) can be derived, and finally we obtain:

$$\mathbf{Z}_{A\mu A\mu'} = \frac{1}{\pi^3}\sum_{\mu''=|\mu-\mu'|}^{\mu+\mu'} B_{\mu''}\left[a(z,M)I_3(\mu,\mu',\mu'') - \frac{1}{\sqrt{2}}I_8(\mu,\mu',\mu'')\right] , \tag{68}$$

$$\mathbf{Z}_{B\mu B\mu'} = \frac{1}{N^B_{\mu}N^B_{\mu'}}\sum_{\mu''=|\mu-\mu'|}^{\mu+\mu'} B_{\mu''}\Big[a(z,M)I_1(\mu,\mu',\mu'') - \frac{a_{\mu'}}{\sqrt{2}}I_2(\mu,\mu',\mu'') + a_{\mu}a_{\mu'}a(z,M)I_3(\mu,\mu',\mu'') - \frac{a_{\mu'}}{\sqrt{2}}I_4(\mu,\mu',\mu'') + a_{\mu}a(z,M)I_5(\mu,\mu',\mu'') - \frac{1}{\sqrt{2}}I_6(\mu,\mu',\mu'') + a_{\mu'}a(z,M)I_7(\mu,\mu',\mu'') - \frac{a_{\mu}a_{\mu'}}{\sqrt{2}}I_8(\mu,\mu',\mu'')\Big] , \tag{69}$$

$$\mathbf{Z}_{A\mu B\mu'} = \frac{1}{\pi^{\frac{3}{2}}N^B_{\mu'}}\sum_{\mu''=|\mu-\mu'|}^{\mu+\mu'} B_{\mu''}\Big[a(z,M)I_5(\mu,\mu',\mu'') - \frac{1}{\sqrt{2}}I_4(\mu,\mu',\mu'') + a_{\mu'}a(z,M)I_3(\mu,\mu',\mu'') - \frac{a_{\mu'}}{\sqrt{2}}I_8(\mu,\mu',\mu'')\Big] . \tag{70}$$

Additionally, by making use of the symmetry of the **Z**-matrix, we obtain

$$\mathbf{Z}_{B\mu' A\mu} = \mathbf{Z}_{A\mu B\mu'} . \tag{71}$$

3 Results and discussion

We have performed practical calculations on some three-body coulomb systems with the method described above. All calculations were carried out on a 4D/25 Personal Iris Silicon Graphics workstation in our laboratory. The programs were written by us.

Some of our calculational results at different μ_m are summarized in Tables 1–4, where μ is the quantum number used to denote the PH basis sets in Sect. 2 and μ_m is the maximum value of it, and we have $\mu_m = \frac{K_m}{2}$ [see Eq. (8), K_m is the maximum global angular momentum]. The unit of energy we used is E_h, which is the abbreviation for the hartree and $1\ E_h = 27.2116eV$.

Now consider Table 1, where we present our calculated results for the ground and the first excited states of the He atom along with the results obtained by Fabre de la Ripelle et al. with their PH method with e-e correlations [4]. In both methods, the mass of the nucleus is treated as infinite. The left two columns in the table are for the ground state, and the right two are for the first excited state. The accurate variational results are also placed in the table for comparison. To achieve convergence, we retain five generalized Laguerre functions for

the ground-state calculations and ten for the first excited state calculations. One can see from Table 1 that, for the ground state, our results are almost the same as those from [4], and for the first excited state, the two sets of results are very similar to each other, particularly at lower μ_m. The comparison validates our method, and we conclude that our method is of the same accuracy as the PH method with e-e correlations of Fabre et al. [4] for the case of helium with infinite nuclear mass.

Table 1. Comparison of energy eigenvalues (E_h) of He atom with infinite nuclear mass calculated by our method with those obtained by Fabre

μ_m[a]	Fabre[b]	us[c]	Fabre[b]	us[d]
	(ground-state)		(2^1S state)	
8	−2.88730	−2.88732	−1.94728	−1.94729
10	−2.89333	−2.89334	−1.99412	−1.99421
14	−2.89876	−2.89876	−2.05111	−2.05113
16	−2.90006	−2.90006	−2.06896	−2.06898
20	−2.90152	−2.90152	−2.09313	−2.09316
24	−2.90226	−2.90226	−2.10815	−2.10816
28	−2.90267	−2.90267	−2.11799	−2.11769
32	−2.90291	−2.90291	−2.12471	−2.12461
36	−2.90307	−2.90307	−2.12946	−2.12923
Variational[e]		−2.90372		−2.14597

[a] $\mu_m = \frac{K_m}{2}$, and K_m is the maximum global angular momentum
[b] Results calculated by Fabre de la Ripelle with their PH method [4]
[c] Our calculated results with five generalized Laguerre functions
[d] Our calculated results with ten generalized Laguerre functions
[e] From Refs. [12–14]

Table 2. Energy eigenvalues of the ground-state for He with finite nuclear mass ($M = 7.2942988 \times 10^3$)($E_h$)

NGLF[b]				
μ_m[a]	1	3	6	7
4	−2.82896	−2.84959	−2.84960	−2.84960
10	−2.85477	−2.89276	−2.89294	−2.89294
16	−2.85789	−2.89933	−2.89965	−2.89965
24	−2.85882	−2.90144	−2.90185	−2.90185
36	−2.85914	−2.90221	−2.90265	−2.90265
50	−2.85924	−2.90244	−2.90290	−2.90290
70	−2.85928	−2.90253	−2.90299	−2.90300
Exact value[c]				−2.90330

[a] $\mu_m = \frac{K_m}{2}$, and K_m is the maximum global angular momentum
[b] The number of generalized Laguerre functions
[c] From Ref. [15]

We report our calculations on the ground and the first excited states (2^1S state) of helium atom with finite nuclear mass ($M = 7.2942988 \times 10^3 m_e$) in Table 2 and Table 3 respectively. The convergency pattern of energy eigen values versus μ_m and NGLF (the number of generalized Laguerre functions) is displayed. From Table 2 we see that the ground-state energy eigenvalues for $NGLF = 6$ are almost the same as those for $NGLF = 7$, which indicates fast and satisfactory convergence for the Laguerre expansion; the eigenvalues increase steadily with μ_m and at $\mu_m = 70$ and with seven GLFs, we get an energy eigenvalue of $-2.90300E_h$, which is in excellent agreement with the exact value of $-2.90330E_h$, reported by Morgan III et al. [15]. On the other hand, Table 3 shows us that, compared with the ground-state, more GLFs are required to obtain good convergence for the excited state. At $\mu_m = 70$ and with ten GLFs, we get an energy value of $-2.14127E_h$, which is very near Drake's result of $-2.14568E_h$ [16].

Our energy results for the ground and the first excited states of $e^+e^-e^+$ are displayed in Table 4. We notice that the convergence pattern is rather good, and compared with our calculations on He mentioned above, more GLFs are required to obtain good convergence. For the ground state, excellent convergence is obtained when the number of GLFs is extended to ten, and at $\mu_m = 65$ and with ten GLFs, we obtain a ground-state energy of $-0.26181E_h$, which is in good agreement with the exact value of $-0.26200E_h$, which was obtained by Frost et al.[17] with the variational method. The convergence for the first excited state is good too, particularly at lower μ_m and at $\mu_m = 65$ and with ten GLFs, we get a energy value of $-0.24175E_h$, but we could not find any results in the literature for this value.

To make a clear comparison, our results for $e^+e^-e^+$ using the full HH basis set (FS) for each μ_m, i.e., all harmonics for $\mu \leq \mu_m$ are retained, are also included in Table 4. These results are obtained by the HH-GLF method [7], which was shown to be as accurate as the best available hyperspherical harmonic method. The errors between the PH results and the FS (full HH set) ones are listed in the last column of Table 4. We can see that the errors are very small, at around $-0.0001E_h$ for both the ground and excited states. Furthermore, the error for the ground-state almost remains constant with the increase of μ_m, and the error for the first excited state decreases with μ_m. This suggests that the error mainly comes from the neglect of harmonics at lower μ_m. The PH calculations performed by Haftel and Mandelzweig

Table 3. Energy eigenvalues of the 2^1S state for He with finite nuclear mass ($M = 7.2942988 \times 10^3$)($E_h$)

NGLF[b]						
μ_m[a]	1	3	5	7	9	10
4	−0.52088	−1.76320	−1.77083	−1.77084	−1.77083	−1.77083
10	−0.54081	−1.91990	−1.99130	−1.99389	−1.99391	−1.99392
16	−0.54445	−1.95001	−2.05632	−2.06817	−2.06869	−2.06869
24	−0.54565	−1.96043	−2.08354	−2.10518	−2.10773	−2.10785
36	−0.54610	−1.96437	−2.09494	−2.12299	−2.12838	−2.12893
50	−0.54623	−1.96558	−2.09864	−2.12924	−2.13631	−2.13727
70	−0.54628	−1.96607	−2.10022	−2.13202	−2.14001	−2.14127
Exact value[c]						−2.14568

[a] $\mu_m = \frac{K_m}{2}$, and K_m is the maximum global angular momentum
[b] The number of generalized Laguerre functions
[c] From Ref. [16]

Table 4. Energy eigenvalues of $e^+e^-e^+(E_h)$

NGLF[b]							
μ_m^a	3	5	7	9	10	FS[c]	error[d]
For the ground-state							
5	−0.24660	−0.24661	−0.24661	−0.24661	−0.24661	−0.24671	−0.00010
10	−0.25615	−0.25660	−0.25660	−0.25660	−0.25660	−0.25672	−0.00012
14	−0.25815	−0.25901	−0.25904	−0.25904	−0.25904	−0.25916	−0.00012
18	−0.25897	−0.26013	−0.26019	−0.26019	−0.26019	−0.26031	−0.00012
24	−0.25947	−0.26086	−0.26098	−0.26099	−0.26099	−0.26111	−0.00012
36	−0.25977	−0.26134	−0.26153	−0.26155	−0.26155		
50	−0.25986	−0.26149	−0.26171	−0.26174	−0.26174		
65	−0.25989	−0.26155	−0.26178	−0.26181	−0.26181		
Exact value[e]					−0.26200		
For the 2^1S state							
5	−0.17025	−0.17374	−0.17374	−0.17374	−0.17374	−0.17387	−0.00013
10	−0.18694	−0.20385	−0.20508	−0.20510	−0.20510	−0.20522	−0.00012
14	−0.19036	−0.21326	−0.21711	−0.21734	−0.21734	−0.21743	−0.00009
18	−0.19176	−0.21775	−0.22403	−0.22492	−0.22495	−0.22503	−0.00008
24	−0.19261	−0.22074	−0.22934	−0.23149	−0.23173	−0.23179	−0.00006
36	−0.19313	−0.22270	−0.23327	−0.23719	−0.23802		
50	−0.19329	−0.22333	−0.23464	−0.23942	−0.24066		
65	−0.19335	−0.22356	−0.23515	−0.24030	−0.24175		

[a] $\mu_m = \frac{K_m}{2}$, and K_m is the maximum global angular momentum
[b] The number of generalized Laguerre functions
[c] The full-set calculational results with 10 generalized Laguerre functions
[d] The difference between the PH results and full-set ones
[e] From Ref. [17]

[3] produced the ground-state energy of $-0.22101E_h$ at $K_m = 12$ for the $e^+e^-e^+$, which has a huge error compared with the full set result of $-0.25040E_h$ [3]. In contrast to this, our PH calculations for $e^+e^-e^+$ are fairly accurate, which indicates that, besides the atomic systems, the PH method can also be very efficient for coulomb systems with particles of comparable mass ratios.

4 Conclusions

Our calculations indicate that the PH method provides an effective means to reduce the degeneracy of the hyperspherical harmonics. It yields very good results for the three-body coulomb systems. The present work also provides us with a good starting point to deal with systems with more particles.

Acknowledgements. This work was supported by the National Natural Science Foundation of the People's Republic of China (Grant No. 29503019).

References

1. Fabre de la Ripelle M (1982) Ann Phys 138:275
2. Fabre de la Ripelle M (1983) Ann Phys 147:281
3. Haftel MI, Mandelzweig VB (1985) Phys Rev C 32:2067
4. Fabre de la Ripelle M, Haftel MI, Larsen SY (1991) Phys Rev A 44:7084
5. Deng CH, Zhang RQ, Feng DC (1993) Int J Quantum Chem 45:385
6. Zhang RQ, Deng CH (1993) Phys Rev A 47:71
7. Bian WS, Deng CH (1994) Int J Quantum Chem 50:395
8. Bian WS, Deng CH (1994) Int J Quantum Chem 51:285
9. Niri Y, Smorodinsky Y (1969) Sov J Nucl Phys 9:515; (1971) Sov J Nucl Phys 12:109
10. Haftel MI, Mandelzweig VB (1989) Ann Phys 189:29; 195:420
11. Edmonds AR (1960) Angular momentum in quantum mechanics. Princeton University Press, Princeton
12. Drake GWF, Yan ZC (1994) Chem Phys Lett 229:486
13. Kleindienst H, Luechow A, Merckens HP (1994) Chem Phys Lett 218:441
14. Kleindienst H, Emrich R (1990) Int J Quantum Chem 37:257
15. Morgan III JD, Baker J (1987) Bull Am Phys Soc 32:1245
16. Drake GWF (1988) Nucl Instrum Methods Phys Res B 31:7
17. Frost AA, Inokuti M, Lowe JP (1964) J Chem Phys 41:482