Fast convergent study on potential-harmonic method of directly solving Schrodinger equation in few-body systems*

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Abstract The correlation-function potential-harmonic and generalized-Laguerre-function expansion method (CFPHGLF) of directly solving the Schrodinger equation in few-body systems is presented and applied to the n^1S ($n = 1 - 4$) states of the helium atom. It can be found that the present eigenenergies for 2^1S, 3^1S and 4^1S states are much better than those from the potential-harmonic and generalized-Laguerre-function method (PHGLF) previously published in Int J Quantum Chem, 1995, 55:47; and that they agree well with the exact Hylleraas CI values. However, the eigenenergy for the ground state 1^1S is not as good as that from the PHGLF method because of omitting the potential harmonic (PH) basis relevent to electron-electron correlation. The results are also simply discussed relative to some other hyperspherical harmonic (HH) and PH methods.

Keywords Hyperspherical coordinates, Potential-harmonic, Fast convergent, Eigenenergy, Helium atom

1 Introduction

The potential-harmonic (PH) method[1] in hyperspherical coordinates is an elegant tool of reducing dramatically the number of the coupled hyperradial differential equations (CHDE) or dimension of the generalized eigenmatrices so as to overcome huge degeneracy of hyperspherical harmonics (HH) and accelerate convergence rate of eigenenergies after all. In 1991, Fabre de la Ripelle[2] began to apply the PH method to the two electron atomic systems, such as H^- and He. Recently, we unified the generalized Laguerre function method (GLF) of directly solving CHDE and PH method into the PHGLF (potential-harmonic and generalized Laguerre function) method by including PH basis of r_{12} (electron-electron distance) as Fabre did[2], and applied it to the n^1S ($n = 1 - 4$) states for the four heliumlike systems, H^-, He, Li^+ and Be^{2+}[3]. Like the results in Ref.[2], the convergent eigenenergies approach those from the complete basis set HH calculation with only a very small discrepancies; however, they are still far from the exact variational Hylleraas CI values except the ground state eigenenergy. The other problem is that inclusion of the PH basis of the electron-electron correlation results in the two linked CHDE. This is equivalent to increasing the number of CHDE by one time. Thus. the size of the eigenmatrix in the PHGLF calculation is not efficiently reduced, especially for the excited states, the eigenenergies of which converge very slowly with the number of GLF. To solve the two problems mentioned here, in this article, by absorbing the idea of the correlation function extensively used to accelerate the convergence of HH expansion, we first modified the PHGLF into a correlation-function PHGLF method hereafter referred to as CFPHGLF method, and then carried out practical calculation on the n^1S ($n = 1 - 4$) states of the helium atom. In addition, we simply discussed the present CFPHGLF results relative to those from some other HH and PH methods.

2 CFPHGLF expansion theory

First, wave function of the heliumlike system is decomposed as

$$\Psi(r_1, r_2, \sigma) = \exp[-Z(r_1 + r_2)]\Phi(r_1, r_2, \sigma) \tag{1}$$

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where $\exp[-Z(r_1+r_2)]$ is the so called correlation function simulating the electron-nucleus cusps completely. Substituting Eq.(1) into the ordinary nonrelativistic Schrodinger equation of the heliumlike systems and introducing the nonregular hyperspherical coordinates[4], one has (in atomic units)

$$\begin{aligned}&[-\tfrac{1}{2}(\frac{\partial^2}{\partial r^2}+\tfrac{5}{r}\frac{\partial}{\partial r}-\frac{\hat{\Lambda}^2(\Omega)}{r^2})+Z(\cos\eta_2+\sin\eta_2)\frac{\partial}{\partial r}\\&+\frac{Z}{r}(\cos\eta_2-\sin\eta_2)\frac{\partial}{\partial\eta_2}+\frac{1}{r_{12}}-(E+Z^2)]\Phi(r,\Omega,\sigma)=0\end{aligned}\tag{2}$$

where $\Omega=(\eta_2,\theta_i,\phi_i)$, r is the hyperradius ($r=r_1^2+r_2^2$, $0\le r\le\infty$) and η_2 ($0\le\eta_2\le\pi/2$) the hyperspherical angle, $\hat{\Lambda}^2(\Omega)$ the grand angular momentum operator, the eigenfunctions of which are the six-dimensional hyperspherical harmonics (HH). For the ^{1}S states ($L=M_L=0$), we let the total wave function

$$\Phi(r,\Omega,\sigma)=[\Phi(r_1,r)+\Phi(r_2,r)]\Theta(\sigma_1,\sigma_2)\tag{3}$$

where Θ is the antisymmetric spin wavefunction, $\Phi(r_1,r)$ and $\Phi(r_2,r)$ are expanded in the individual PH basis $P^0_{2k}(\Omega,0)$ and $P^0_{2k}(\Omega,\pi/2)$ defined by Fabre de la Ripelle[1] for functions of r_1 and r_2, respectively,

$$\Phi(r_1,r)=\Sigma_k F_k(r)P^0_{2k}(\Omega,0)\tag{4a}$$

$$\Phi(r_2,r)=\Sigma_k F_k(r)P^0_{2k}(\Omega,\pi/2)\tag{4b}$$

Since $P^0_{2k}(\Omega,0)$ and $P^0_{2k}(\Omega,\pi/2)$ differ trivially by only a phase factor $(-1)^k$, we obtain

$$\Phi(r,\Omega,\sigma)=\Sigma_k F_k(r)P^0_{2k}(\Omega,0)\Theta(\sigma_1,\sigma_2),\qquad(k=\text{even})\tag{5}$$

Substituting the expansion into Eq.(2), and considering the orthonormal relationship of the PH basis and spin functions $\Theta(\sigma_1,\sigma_2)$, we get the coupled hyperradial differential equations

$$\begin{aligned}&\{-\tfrac{1}{2}[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\tfrac{5}{r}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{2k(2k+4)}{r^2}]-(E+Z^2)\}F_k(r)\\&+\Sigma_{k'}[ZA_{kk'}\frac{\mathrm{d}}{\mathrm{d}r}+\tfrac{1}{r}D_{kk'}]F_{k'}(r)=0\end{aligned}\tag{6}$$

where

$$A_{kk'}=<P^0_{2k'}(\Omega,0)\mid(\cos\eta_2+\sin\eta_2)\mid P^0_{2k}(\Omega,0)>\tag{7a}$$

$$D_{kk'}=<P^0_{2k'}(\Omega,0)\mid Z(\cos\eta_2-\sin\eta_2)\frac{\partial}{\partial\eta_2}+\frac{r}{r_{12}}\mid P^0_{2k}(\Omega,0)>\tag{7b}$$

Eq.(6) has the similar form to that from the correlation-function hyperspherical-harmonic and generalized Laguerre function (CFHHGLF) method[5]. Consequently, it can also be directly solved by the GLF method of hyperradial wave function, which has been described elsewhere[4-6].

To perform numerical calculation, we give the analytical expressions of the matrix elements $A_{kk'}$ and $D_{kk'}$ below derived through making use of coupled relationship and definition of the PH basis[1].

$$\begin{aligned}A_{kk'}=&\frac{-64}{\pi}\Sigma_{k''=\text{even}}\frac{(k''+1)}{(2k''-1)(2k''+1)(2k''+3)(2k''+5)}\\&(k''=\mid k-k'\mid,\mid k-k'\mid+2,\cdots,k+k')\end{aligned}\tag{8}$$

$$<P^0_{2k'}(\Omega,0)\mid\frac{r}{r_{12}}\mid P^0_{2k}(\Omega,0)>=\frac{8\sqrt{2}}{\pi}\Sigma_{k''}\frac{(-1)^{k''/2}}{(2k''+1)(2k''+3)}\tag{9}$$

with $k'' = \mid k - k' \mid, \mid k - k' \mid +2, \cdots, k + k'$; k, k' having the same parity.

$$\begin{aligned} &< P^0_{2k'}(\Omega, 0) \mid (\cos\eta_2 - \sin\eta_2)\tfrac{\partial}{\partial\eta_2} \mid P^0_{2k}(\Omega, 0) > \\ &= -\frac{(k+2)!(k'+1)!}{\sqrt{2}\Gamma(k+3/2)\Gamma(k'+3/2)} C(1; k-1, 3/2, 3/2; k', 1/2, 1/2) \end{aligned} \tag{10}$$

where

$$\begin{aligned} &C(t; n, a, b; m, r, s) = \int_{-1}^{1} \mathrm{d}x (1-x)^t (1+x)^b P_n^{a,b}(x) P_m^{r,s}(x) \\ &= \frac{2^{b+t+1}\Gamma(a-t+n)\Gamma(b+n+1)\Gamma(r+m+1)\Gamma(t+1)}{m!n!\Gamma(r+1)\Gamma(a-t)\Gamma(b+t+n+2)} \\ &\times {}_4F_3(-m, r+s+m+1, t+1, t-a+1; r+1, b+t+n+2, t-a-n+1; 1) \end{aligned} \tag{11}$$

Hence, $D_{kk'}$ can be simply calculated from Eqs.(9,10). The analytical expressions of related matrix elements $A_{kk'}$, $D_{kk'}$ in the CFPHGLF scheme are much simpler than in the CFHHGLF one.

3 Results and discussions

The CFPHGLF method was applied to the n^1S ($n = 1 - 4$) states of the helium atom. All the calculations are performed on the IRIS SGI workstation with programs written by us. The results are summarized in Table 1 together with those from the PHGLF[3], CFHHGLF[5]

Table 1 Eigenenergies ($-E$/u) of the n^1S ($n = 1 - 4$) states for helium atom calculated from the CFPHGLF method[a]

	NPH	4	6	8	10	4	6	8	10
NGLF	NHH	16	36	64	100	16	36	64	100
	λ_2	12	20	28	36	12	20	28	36
		1^1S				2^1S			
24		2.879418	2.879096	2.879046	2.879034	2.144328	2.144373	2.144271	2.144166
32		2.879418	2.879096	2.879047	2.879034	2.144326	2.144359	2.144257	2.144147
40		2.879418	2.879096	2.879046	2.879034	2.144325	2.144358	2.144257	2.144146
50		2.879418	2.879096	2.879046	2.879034	2.144327	2.144358	2.144257	2.144147
60		2.879417	2.879096	2.879046	2.879045	2.144325	2.144358	2.144255	2.144146
PHGLF[b]		—	—	—	2.900935	—	—	—	2.081632
CFHHGLF[c]		—	2.903737	—	—	—	2.146033	—	—
HCI[7]		—	—	—	2.903724	—	—	—	2.145974
		3^1S				4^1S			
24		2.042746	2.059051	2.059324	2.059126	1.971942	2.026706	2.028604	2.028339
32		2.043136	2.060249	2.060667	2.060473	1.966948	2.026025	2.032836	2.032766
40		2.043148	2.060330	2.060785	2.060593	1.966710	2.025235	2.032055	2.033312
50		2.043138	2.060331	2.060795	2.060602	1.966713	2.025151	2.032886	2.033249
60		2.043142	2.060333	2.060798	2.060644	1.966713	2.025147	2.032859	2.033215
PHGLF[b]		—	—	—	1.827216	—	—	—	1.533855
CFHHGLF[c]		—	2.060659	—	—	—	2.026797	—	—
HCI[7]		—	—	—	2.061271	—	—	—	2.033586

Notes: a. NPH, NHH and NGLF represent the number of potential harmonics, the number of all hyperspherical harmonics at the given grand angular momentum λ_2, the number of the generalized Laguerre functions, respectively. $\lambda_2 = 2k$. b. From Ref.[4], NGLF=7, $\Phi(r, \Omega, \sigma) = [\Phi(r_1, r) + \Phi(r_2, r + \Phi(r_{12}, r)]\Theta(\sigma_1, \sigma_2)$, c. From Ref.[6], NGLF=32, the correlation function is $\exp[-Z(r_1 + r_2)]$.

and the Hylleraas variational CI (HCI)[7] values. Table 1 shows that the ground state eigenenergy deviates markedly from the HCI result (−2.87903 vs −2.90372 u), while the eigenenergies for the three excited states 2^1S, 3^1S and 4^1S near the HCI ones, the errors of which are only 0.001828, 0.000627 and 0.000371 u, respectively. Table 1 also shows that the present eigenenergies for the excited

sates n^1S ($n = 2 - 4$) are much better than those from the PHGLF, while the eigenenergy for the ground state is not as good as that from the PHGLF. This clearly indicates that, in the PH expansion scheme, only electron-nucleus correlation is not enough, and the electron-electron (e-e) correlation seems to be absolutely essential to get accurate ground state eigenenergy. In the case of the excited states, the electron-nucleus cusps play more important role than the e-e correlation and the cluster structure in accelerating convergence of eigenenergies. According to Table 1, the eigenenergy of the ground state also deviates appreciably from that by the CFHHGLF method of complete set expansion in the angular part with the same correlation function as the CFPHGLF method, but those two methods yield almost the same results for the excited states 2^1S, 3^1S and 4^1S, at the given λ_2, which have discrepancies only in the fourth decimal place for 2^1S, fifth decimal place for 3^1S and 4^1S. This implies that the accuracy loss caused by the PH approximation for the ground state 1^1S is much higher than those for the excited states. To some extent, it may be responsible for the fact that the contribution from the hyperspherical harmonic basis except the PH are much smaller to these excited states than to the ground state. As far as the energy precision is only concerned, the CFPHGLF method is not as good as the CFHHGLF method, as if the general PH method is inferior to the HH method because of omitting the HH basis that do not appear in the expansion of the interparticle potential. However the size of generalized eigenmatrices is dramatically reduced from $(\mathrm{NHH}\times\mathrm{NGLF})^2$ in CFHHGLF to $(\mathrm{NPH}\times\mathrm{NGLF})^2$ in the CFPHGLF method.

In sum, the CFPHGLF method modified from PHGLF through introducing radial correlation function generates very accurate eigenenergies for excited states n^1S ($n = 2 - 4$) of the helium atom, which only have errors in the fourth decimal place for 2^1S, fifth decimal place for 3^1S and 4^1S states compared with the exact variational values and the complete set expansion CFHHGLF results. The ground state eigenenergy is not so good. The present results implies that electron-nucleus cusp plays more important role than the electron-electron cusp and the cluster structure for the loosely bound excited states, and that electron-electron cusp is absolutely essential for the tightly bound ground state. Moreover the results tell us that the contribution from the hyperspherical harmonic basis except the PH are much smaller to these excited states than to the ground state.

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