Eur. Phys. J. D **19**, 9–12 (2002)
DOI: 10.1140/epjd/e20020049

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Numerical calculation of energies of some excited states in a helium atom

B. Duan[a], X.-Y. Gu, and Z.-Q. Ma

CCAST (World Laboratory), P.O. Box 8730, Beijing 100080, P.R. China
and
Institute of High Energy Physics, Beijing 100039, P.R. China

Received 27 May 2001 and Received in final form 20 November 2001

Abstract. The energies of some excited states with the total angular momentum $L = 0$, 1 and 2, the total spin of two electrons $S = 0$ and 1, and the even and odd parities are precisely calculated directly from the Schrödinger equation where the mass of the helium nucleus is finite. Moreover, we find that the solutions to the equation for the excited states have some more nodes, which can be used to distinguish the states with the same spectral term.

PACS. 03.65.Ge Solutions of wave equations: bound states – 32.30.-r Atomic spectra

1 Introduction

A helium atom is a typical Coulomb three-body system with strong correlated motion of two electrons. The numerical calculation of the energy levels and the wave functions of a helium atom is one of the most interesting and fundamental problems in the atomic physics. The variational methods can achieve very high precision for energy values [1–3]. However, the difficulty in choosing the variational functions is aggravated for the excited states, especially for the party $(-1)^{\ell+1}$. It was recognized rather early that the naive hyperspherical harmonic (HH) method has very limited accuracy. Various efforts have been devoted to overcome the substantial drawbacks in the naive HH method [4–8], such as the correlation function HH method [9–13], the hyperspherical coordinate method [14–17], the method of complex coordinate rotations [18–20], the R-matrix method [21] and so on.

In our previous papers [23–27] we presented a new method to calculate the energy levels of a quantum three-body system, where the motion of the center of mass and the global rotation of the system are completely separated from the internal motion. Only three internal variables are involved in both the generalized radial functions and equations. The internal variables are chosen as the hyperradius ρ and two dimensionless η and ζ to make the potential a meromorphic function [28]. Expanding the wave function by a series of η and ζ, we obtain an ordinary differential matrix equation with respect to the hyperradius ρ. We have precisely calculated the lowest energies for some spectral terms ${}^{2S+1}L^{\mathrm{e(o)}}$ of a helium atom in our previous papers [25,26]. Since the solution to the ordinary differential matrix equation with respect to the hyperradius ρ has no node for the bound state with the lowest energy in a spectral term, in the calculation the series converges very fast. However, there exist some nodes for the excited states, which slow down the convergence of the series in calculation. In the present paper we directly calculate by both the propagation matrix $F(\rho)$ and its inverse matrix $G(\rho)$ to bypass the nodes and to obtain the energy levels for some excited states, where the total orbital angular momentum L is 0, 1 and 2, the total spin S is 0 and 1, and the parity is even and odd.

The plan of this paper is as follows. We will sketch the method in Section 2 [25–27] and calculate the energy levels of some excited states in Section 3. The summary and discussion is given in Section 4.

2 The method

After removing the motion of the center of mass and the global rotation, the Schrödinger equation for a helium atom reduces to the generalized radial equations [26]

$$\Psi_\ell^{\ell\lambda}(\mathbf{x},\mathbf{y}) = \sum_{q=\lambda}^{\ell} \psi_q^{\ell\lambda}(\xi_1,\xi_2,\xi_3) Q_q^{\ell\lambda}(\mathbf{x},\mathbf{y}), \tag{1}$$

$$\begin{aligned} &\Delta\psi_q^{\ell\lambda} + 4q\partial_{\xi_1}\psi_q^{\ell\lambda} + 4(\ell-q+\lambda)\partial_{\xi_2}\psi_q^{\ell\lambda} \\ &+ 2(q-\lambda)\partial_{\xi_3}\psi_{q-1}^{\ell\lambda} + 2(\ell-q)\ \partial_{\xi_3}\psi_{q+1}^{\ell\lambda} \\ &\qquad = -2(E-V)\psi_q^{\ell\lambda}, \qquad \lambda \le q \le \ell, \qquad \lambda = 0,\ 1, \end{aligned} \tag{2}$$

$$\begin{aligned} \Delta\psi_q^{\ell\lambda}(\xi_1,\xi_2,\xi_3) = &\left\{4\xi_1\partial_{\xi_1}^2 + 4\xi_2\partial_{\xi_2}^2 + (\xi_1+\xi_2)\,\partial_{\xi_3}^2 \right. \\ &\left. +4\xi_3\left(\partial_{\xi_1}+\partial_{\xi_2}\right)\partial_{\xi_3} + 6\left(\partial_{\xi_1}+\partial_{\xi_2}\right)\right\}\psi_q^{\ell\lambda}(\xi_1,\xi_2,\xi_3), \end{aligned}$$

---

[a] e-mail: `duanb@mail.ihep.ac.cn`

where $\mathbf{x}$ and $\mathbf{y}$ are the Jacobi coordinate vectors, $\xi_1 = \mathbf{x}\cdot\mathbf{x}$, $\xi_2 = \mathbf{y}\cdot\mathbf{y}$ and $\xi_3 = \mathbf{x}\cdot\mathbf{y}$ are the internal variables, and $Q_q^{\ell\lambda}(\mathbf{x},\mathbf{y})$ are the generalized harmonic polynomials

$$Q_q^{\ell\lambda}(\mathbf{x},\mathbf{y}) = \frac{(x_1+\mathrm{i}x_2)^{q-\lambda}(y_1+\mathrm{i}y_2)^{\ell-q}}{(q-\lambda)!(\ell-q)!} \times \left\{(x_1+\mathrm{i}x_2)y_3 - x_3(y_1+\mathrm{i}y_2)\right\}^{\lambda}\cdot \tag{3}$$

In order to improve the convergence of the series, we define new internal variables (ρ, η, ζ) to make V a meromorphic function [28]

$$\begin{aligned}
\rho &= (\xi_1+\xi_2)^{1/2}, \qquad \eta = \frac{r_{23}}{\rho} = \left(\frac{2\xi_2}{\xi_1+\xi_2}\right)^{1/2}, \\
\zeta &= \frac{r_{12}}{\rho} + \frac{r_{13}}{\rho} \\
&= \left\{\frac{(M+2)\xi_1 + M\xi_2 + 2\left[M(M+2)\right]^{1/2}\xi_3}{2M\left(\xi_1+\xi_2\right)}\right\}^{1/2} \\
&\quad + \left\{\frac{(M+2)\xi_1 + M\xi_2 - 2\left[M(M+2)\right]^{1/2}\xi_3}{2M\left(\xi_1+\xi_2\right)}\right\}^{1/2},
\end{aligned} \tag{4}$$

$$V = -\frac{2\zeta}{\rho p} + \frac{1}{\rho\eta}, \qquad p = \frac{\eta^2 + M\zeta^2 - M - 2}{2M}\cdot \tag{5}$$

Since the total wave function has to be antisymmetric in the permutation of two electrons, the spatial wave function Ψ is symmetric when $S = 0$ and antisymmetric when $S = 1$. Because all new internal variables ρ, η and ζ remain invariant in the permutation of two electrons, we have to introduce a variable s, which changes its sign in the permutation, to construct the wave function with the right property in the permutation:

$$s = \frac{r_{12}}{\rho} - \frac{r_{13}}{\rho} = \frac{2\xi_3}{\rho^2\zeta}\left(\frac{M+2}{M}\right)^{1/2}\cdot \tag{6}$$

$$\Psi_\ell^{(S)\ell\lambda}(\mathbf{x},\mathbf{y}) = \sum_{q=\lambda}^{\ell} \phi_q^{(S)\ell\lambda}(\rho,\eta,\zeta)s^{\delta(q)}Q_q^{\ell\lambda}(\mathbf{x},\mathbf{y})/\rho^{\ell+\lambda}, \tag{7}$$

$$\delta(q) = \begin{cases} 0 & \text{when } \ell - q + \lambda - S \text{ is even} \\ 1 & \text{when } \ell - q + \lambda - S \text{ is odd} \end{cases}$$

Now, we rewrite the generalized radial functions $\phi_q^{(S)\ell\lambda}(\rho,\eta,\zeta)$ as an $(\ell-\lambda+1)\times 1$ matrix $\phi^{(S)\ell\lambda}(\rho,\eta,\zeta)$, satisfying the coupled partial differential equations

$$\left(\partial_\rho^2 + \frac{5}{\rho}\partial_\rho + \frac{4\Lambda^{(S)\ell\lambda}}{\rho^2}\right)\phi^{(S)\ell\lambda}(\rho,\eta,\zeta) = -2(E-V)\phi^{(S)\ell\lambda}(\rho,\eta,\zeta), \tag{8}$$

where $S = 0$ or 1, and $\lambda = 0$ or 1, and $\Lambda^{(S)\ell\lambda}$ is an $(\ell-\lambda+1)$-dimensional matrix differential operator. One can find the explicit forms for $\Lambda^{(S)\ell\lambda}$ in our previous papers [25,26]. In the calculation of equation (8) which describes the internal motions of a helium atom with the given total spin S, the total angular momentum quantum number ℓ and the parity $(-1)^{\ell+\lambda}$, we expand $\phi^{(S)\ell\lambda}$ by a series as $\eta^a\zeta^b$ and truncate the series at the degree N, the highest sum of exponents. The coefficients are the functions only depending on the hyperradius ρ. In order to derive the equations, it is necessary to calculate the matrix elements of the operators Λ and V between the basis functions. We first calculate the Jacobi determinant $J(\eta,\zeta)$ for the replacement of variables from $\mathbf{x},\mathbf{y}$ to ρ,η,ζ and the Euler angles. Then, we integer over the Euler angles and obtain the weight functions $g^{(S)\ell\lambda}$ [25,26]. At last, we change the basis functions $\eta^a\zeta^b$ by the Schmidt method and similarity transformation to the orthogonal basis $B_m^{(S)\ell\lambda}(\eta,\zeta)$ satisfying

$$\begin{aligned}
&\int_\Omega\int \mathrm{d}\eta\mathrm{d}\zeta J(\eta,\zeta)B_m^{(S)\ell\lambda}(\eta,\zeta)^\dagger \\
&\qquad \times g^{(S)\ell\lambda}B_{m'}^{(S)\ell\lambda}(\eta,\zeta) = \delta_{mm'}, \\
&\int_\Omega\int \mathrm{d}\eta\mathrm{d}\zeta J(\eta,\zeta)B_m^{(S)\ell\lambda}(\eta,\zeta)^\dagger \\
&\qquad \times g^{(S)\ell\lambda}\Lambda^{(S)\ell\lambda}B_{m'}^{(S)\ell\lambda}(\eta,\zeta) = \delta_{mm'}\Lambda_{mm}^{(S)\ell\lambda}, \\
&\int_\Omega\int \mathrm{d}\eta\mathrm{d}\zeta J(\eta,\zeta)B_m^{(S)\ell\lambda}(\eta,\zeta)^\dagger \\
&\qquad \times g^{(S)\ell\lambda}VB_{m'}^{(S)\ell\lambda}(\eta,\zeta) = V_{mm'}^{(S)\ell\lambda}(\rho),
\end{aligned} \tag{9}$$

where $\Lambda_{mm}^{(S)\ell\lambda}$ and $\rho V_{mm'}^{(S)\ell\lambda}$ do not depend on ρ.

The functions $\phi^{(S)\ell\lambda}(\rho,\eta,\zeta)$ now are expanded with respect to the basis $B_m^{(S)\ell\lambda}(\eta,\zeta)$, where the coefficients $R_m^{(S)\ell\lambda}(\rho)$ are the hyperradial functions depending on the hyperradius ρ. Since the matrix for the potential V is non-diagonal, we rewrite the functions as a column matrix $R^{(S)\ell\lambda}(\rho)$, satisfying the following matrix equation

$$\begin{aligned}
&\left(\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{5}{\rho}\frac{\mathrm{d}}{\mathrm{d}\rho} + \frac{4\Lambda^{(S)\ell\lambda}}{\rho^2}\right)R^{(S)\ell\lambda}(\rho) = \\
&\qquad -2\left[E - V^{(S)\ell\lambda}(\rho)\right]R^{(S)\ell\lambda}(\rho), \\
&\qquad S = 0 \text{ or } 1, \qquad \lambda = 0 \text{ or } 1.
\end{aligned} \tag{10}$$

Equation (10) is a second-order ordinary differential equation, and its solutions corresponding to the excited states have some nodes. As done in references [25,26,28], we solve the propagation matrix $F^{(S)\ell\lambda}(\rho)$ instead of the hyperradial function $R^{(S)\ell\lambda}(\rho)$ directly:

$$\rho\frac{\mathrm{d}}{\mathrm{d}\rho}R^{(S)\ell\lambda}(\rho) = F^{(S)\ell\lambda}(\rho)R^{(S)\ell\lambda}(\rho). \tag{11}$$

Substituting equation (11) into equation (10), we obtain

$$\rho\frac{\mathrm{d}F^{(S)\ell\lambda}(\rho)}{\mathrm{d}\rho} + F^{(S)\ell\lambda}(\rho)^2 + 4F^{(S)\ell\lambda}(\rho) = -4\Lambda^{(S)\ell\lambda} - 2\left[E - V^{(S)\ell\lambda}(\rho)\right]\rho^2, \tag{12}$$

and the boundary condition:

$$F^{(S)\ell\lambda}(0)^2 + 4F^{(S)\ell\lambda}(0) = \Lambda^{(S)\ell\lambda}. \tag{13}$$

Table 1. The numerical calculation for the energy levels of some excited states in a helium atom (in the atomic unit).

Spectral term	No. of	Numerical results for E		Observation
$^{2S+1}L^{\rm e(o)}$	nodes	Our results	Other results [29,30]	[33,34]
$1s^2$ $^1\rm S^e$	0	2.9033045555601	2.9033045556	2.90338629[a]
$1s2s$ $^1\rm S^e$	1	2.145678575	2.1456785860	2.14577009
$1s3s$ $^1\rm S^e$	2	2.06095295	2.0609890809	2.06107971
$1s4s$ $^1\rm S^e$	3	2.031218	2.0333078175	2.03339816
$1s2s$ $^3\rm S^e$	0	2.174930188	2.1749301891	2.17502843
$1s3s$ $^3\rm S^e$	1	2.0683993	2.0684052422	2.06849761
$1s4s$ $^3\rm S^e$	2	2.035420	2.0362328278	2.03632385
$1s2p$ $^1\rm P^o$	0	2.123545643	2.1235455653	2.12363788
$1s3p$ $^1\rm P^o$	1	2.05483507	2.0548626607	2.05495355
$1s4p$ $^1\rm P^o$	2	2.029143	2.0307903858	2.03088085
$1s2p$ $^3\rm P^o$	0	2.132880637	2.1328806406	2.13296985
$1s3p$ $^3\rm P^o$	1	2.05778447	2.0578016	2.05789149
$1s4p$ $^3\rm P^o$	2	2.0307414	2.0320468	2.03213691
$2p3p$ $^1\rm P^e$	0	0.5801657683	0.580165768	0.58016394[b]
$2p4p$ $^1\rm P^e$	1	0.5399670	0.5399672	
$2p^2$ $^3\rm P^e$	0	0.7103966457	0.710396457	0.71084835[c]
$2p3p$ $^3\rm P^e$	1	0.5677868	0.56773387	
$1s3d$ $^1\rm D^e$	0	2.05530605	2.055338994	2.05542923
$1s4d$ $^1\rm D^e$	1	2.0288772	2.0310014	2.03109162
$1s3d$ $^3\rm D^e$	0	2.0553229	2.055354585	2.05544481
$1s4d$ $^3\rm D^e$	1	2.0289701	2.0310104	2.03110061
$2p3d$ $^1\rm D^o$	0	0.5637256		
$2p4d$ $^1\rm D^o$	1	0.5345003		
$2p3d$ $^3\rm D^o$	0	0.5592482		
$2p4d$ $^3\rm D^o$	1	0.5325974		

[a] Reference [33], [b] references [32–34], [c] references [32–36].

For a given energy $E = -\epsilon$, we can numerically calculate the matrix $F^{(S)\ell\lambda}(\rho)$ from equations (12, 13) by the method of analytic continuation. Namely, at a given position ρ and the length of step $\varDelta\rho$ (say 0.1) we calculate $F^{(S)\ell\lambda}(\rho + \varDelta\rho)$ by the Taylor series until the sum of the square elements of the next last term becomes less than 10^{-10} and that of the last term is smaller. If the term of $(\varDelta\rho)^{22}$ could not satisfy this condition, we will decrease the length of step. If the condition still could not be satisfied, it means a node appears and we calculate the inverse matrix $G^{(S)\ell\lambda}(\rho) = F^{(S)\ell\lambda}(\rho)^{-1}$ instead. We also check the eigenvalues of $F^{(S)\ell\lambda}(\rho)$ to see whether one of them becomes negative infinity (big number) and jumps to positive infinity and to make sure a node occurs. As ϵ decreases, if we find the number of nodes increases by one, it means a bound state occurs. The energy of the bound state is equal to $-\epsilon$ where the additional node goes to infinity, and can be calculated by dichotomy.

3 Calculation results

By the method introduced in the preceding section we calculate the energy levels E of some excited states of a helium atom, where the angular momentum $L = 0$, 1 and 2, the total spin of two electrons $S = 0$ and 1, and the parity is even and odd, directly from the Schrödinger equation (2), where $M = 7294.2618241$. The results are listed in Table 1. The convergence of the series in our numerical calculation is fast, where the highest degree N of the series is taken to be 9 for the case of $\ell = 2$, $\lambda = 0$ and 10 for the others.

For comparison, we also list in Table 1 the results of other calculations [29–31] and the observations [32–36]. Since the relativistic effect and the spin-orbital interaction were neglected in equation (1), the calculation error in the order of magnitude $(137)^{-2} \sim 10^{-4}$ is reasonable in comparison with the observation values. As seen from the Table 1, our calculation results of the lowest energy levels in each spectral term are almost the same as that of references [29–31]. This shows this methods is effective in the calculations of the lowest energy levels in each spectral term. But as the number n of the nodes increases, the quality of our results deteriorate. This suggests that a larger N should be taken to reach the same accuracies as that of the lowest energy levels in each spectral term. The other distinguishing feature is that our results of these spectral terms, where $\lambda = 1$, are very accurate even if N is very small. This indicates that the basis functions $B_m^{(S)\ell\lambda}(\eta,\zeta)$ match with the real wave functions.

4 Summary and discussion

In this paper, we present a numerical method to calculate the energy levels of some excited states of a helium atom directly from the Schrödinger equation with a finite mass of the nucleus. The motions of the center of mass and the global rotation of the system are separated completely from the internal motion, so that only three internal variables are involved in both the functions and the equations. By making use of the right internal variables ρ, η, and ζ, the potential becomes a meromorphic function of internal variables. Expanding the functions as a series in η and ζ, and truncating the series at the degree N, we obtain a finite set of the coupled ordinary differential equations with respect to the hyperradius ρ. Given an energy $-\epsilon$, we propagate $F^{(S)\ell\lambda}(\rho)$ or $G^{(S)\ell\lambda}(\rho)$ to infinity and count the corresponding number $n(\epsilon)$ of the nodes. With the help of the dichotomy, we calculate the energy levels and the number of nodes of some excited states in a helium atom listed in Table 1.

The advantages of our method are as follows. First, the number of basis functions $Q_q^{\ell\lambda}(\mathbf{x},\mathbf{y})$ for the angular momentum quantum number ℓ and the parity $(-1)^{\ell+\lambda}$ is a finite number $(\ell+1-\lambda)$. The contribution from the remaining partial angular momentum states is incorporated into that from the generalized radial functions. Second, we choose the internal variables (ρ,η,ζ) to make the Coulomb potential a meromorphic function. This choice improves the convergence of the series in calculation. At last, our method is simple for calculating the energy levels of excited states in a same spectral term, where the matrices $\Lambda^{(S)\ell\lambda}$ and $V^{(S)\ell\lambda}$ are the same. As the energy increases, the number of the nodes in the hyperradial function increases, just like it occurs in a hydrogen atom. We guess and believe a generalized Sturm-Liouville theorem holds in a quantum three-body problem. We will discussed it elsewhere.

Our method is also suitable for some other Coulomb three-body systems, such as helium-like ion (H^- and Li^+ etc.) and positronium negative ion [27], where the mass ratio M is very large or equal to one. We are trying to study the system with a very small M, such as the hydrogen molecule ion elsewhere.

This work was supported by the National Natural Science Foundation of China.

References

1. D.E. Freund, B.D. Huxtable, J.D. Morgan III, Phys. Rev. A **29**, 980 (1984).
2. V.I. Korobov, Phys. Rev. A **61**, 064503 (2000).
3. B. Schiff, H. Lifson, C.L. Pekeris, P. Rabinowitz, Phys. Rev. A **140**, 1104 (1965).
4. R. Krivec, Few-Body Syst. **25**, 199 (1998).
5. U. Fano, D. Green, J.L. Bohn, T.A. Heim, J. Phys. B **32**, R1 (1999).
6. V.B. Mandelzweig, Nucl. Phys. A **508**, 63c (1990).
7. M. Viviani, Few-Body Systems **25**, 177 (1998).
8. C.D. Lin, Phys. Rep. **257**, 1 (1995).
9. M.I. Haftel, V.B. Mandelzweig, Ann. Phys. **189**, 29 (1989).
10. M.I. Haftel, V.B. Mandelzweig, Phys. Lett. A **120**, 232 (1987).
11. M.I. Haftel, V.B. Mandelzweig, Phys. Rev. A **38**, 5995 (1988).
12. N. Barnea, V.B. Mandelzweig, Phys. Rev. A **41**, 5209 (1990).
13. N. Barnea, V.B. Mandelzweig, Phys. Rev. A **44**, 7053 (1991).
14. J.Z. Tang, S. Wantanabe, M. Matsuzawa, Phys. Rev. A **46**, 2437 (1992).
15. B. Zhou, C.D. Lin, J.Z. Tang, S. Watanabe, M. Matsuzawa, J. Phys. B **26**, 2555 (1993).
16. B. Zhou, C.D. Lin, J. Phys. B **26**, 2575 (1993).
17. T.A. Herm, D. Green, J. Math. Phys. **40**, 2162 (1999).
18. Y.K. Ho, J. Phys. B **15**, L691 (1982).
19. Y.K. Ho, Phys. Rev. A **34**, 4402 (1986).
20. A. Buegers, D. Wintgen, J.M. Rost, J. Phys. B **28**, 3163 (1995).
21. J. Yan, Y.Z. Qu, V. Voky, J.M. Li, Phys. Rev. A **57**, 997 (1998).
22. P. Selles, J. Mazeau, A. Huetz, J. Phys. B **20**, 5183 (1987).
23. Z.Q. Ma, Sci. Chin. A **43**, 1093 (2000).
24. X.Y. Gu, B. Duan, Z.Q. Ma, Phys. Lett. A **281**, 168 (2001).
25. B. Duan, X.Y. Gu, Z.Q. Ma, Phys. Lett. A **283**, 229 (2001).
26. B. Duan, X.Y. Gu, Z.Q. Ma, Phys. Rev. A **64**, 012102 (2001).
27. B. Duan, X.Y. Gu, Z.Q. Ma, Chin. Phys. Lett. **18**, 854 (2001).
28. S.N. Tan, Commun. Theor. Phys. **35**, 71 (2001).
29. G.W.F. Drake, *Atomic Molecular and Optical Physics Handbook* (American Institute of physics, New York, 1996); G.W.F. Drake, Z.C. Yan, Phys. Rev. A **46**, 2378 (1992).
30. M. Hesse, D Baye, J. Phys. B: At. Mol. Opt. Phys. **34**, 1425 (2001).
31. G.W.F. Drake, A. Dalgarno, Phys. Rev. A **1**, 1325 (1970).
32. H.G. Berry, I. Martinson, L.J. Curtis, L. Lundin, Phys. Rev. A **3**, 1934 (1970).
33. A.A. Radzig, B.M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer Series in Chemical Physics 31, Springer-verlag Berlin, 1985), Chaps. 6 and 7.
34. NIST Atomic Spectra Database Levels Data He I, `http://physics.nist.gov/ cgi-bin/AtData /main_asd`.
35. P.G. Kruger, Phys. Rev. **36**, 855 (1930).
36. K.T. Compton, J.C. Boyce, J. Franklin Inst. **205**, 497 (1928).