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RESEARCH ARTICLE

LIU Qiang, KANG Shuai, ZHANG Xian-zhou, SHI Ting-yun

Hydrogen atom in strong magnetic field: a high accurate calculation in spheroidal coordinates

Abstract A B-spline-type basis set method for the calculation of hydrogen atom in strong magnetic fields in the frame of spheroidal coordinates has been introduced. High accurate energy levels of hydrogen in the magnetic field, with strength ranging from 0 to 1000 a.u., have been obtained. For the ground state, $1s_0$, energies with at least 11 significant digits have been obtained. For the low-lying excited state, $2p_{-1}$, energies with at least 9 significant digits are obtained. The method has also been applied to the calculation of hydrogen Rydberg states in laboratory magnetic fields. Energy spectra with at least 10 significant digits are presented. A comparison with other results in the literatures has been performed. Our results are comparable to the most accurate one up to date. A possible extension to the cases of parallel and crossed electric and magnetic fields have been discussed.

Keywords hydrogen atom, strong magnetic field, spheroidal coordinates, B-spline, energy spectra

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LIU Qiang, KANG Shuai, SHI Ting-yun (✉)
State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences, Wuhan 430071, China
E-mail: tyshi@wipm.ac.cn

LIU Qiang, ZHANG Xian-zhou
College of Physics and Information Engineering, Henan Normal University, Xinxiang 453002, China

KANG Shuai
Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

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1 Introduction

The hydrogen atom in a strong magnetic field is one of the fundamental quantum-mechanical problems. In the range of experimental magnetic fields (from 0 to several tens Tesla), diamagnetic interaction between atom and magnetic field could be negligible compared to Zeeman term and Coulomb interaction for low-lying states of atom [1]. The spherical symmetry of the central force field is approximately retentive. Perturbation theory can give a satisfactory explanation for experimental results. When the diamagnetic interaction is compared with Coulomb interactions between an electron and nucleus, such as highly excited Rydberg atoms in an experimental magnetic field, the atom in a white dwarf and neutron star, and exciton or impurities in semiconductor materials, the perturbation theory is no longer applicable [2]. A non-perturbation theory should be developed. Due to the importance of the diamagnetic hydrogen problem in understanding the basic scientific problems such as quantum chaos and quantum-class correspondence, as well as in potential applications in astrophysics and solid state physics, various approximate methods have been developed to solve this simple variable nonseparable system in past three decades.

For the calculation of the low-lying states of a hydrogen atom in an ultra-high magnetic field (10^5–10^9 T), which is the case for atoms in the atmosphere of white dwarfs and neutron stars, existent effective methods includes basis set method using different basis functions [3－8], eigenvalue analysis method [9－11], finite element method [12], adiabatic approximate method [13－15], and series method [16－18]. Among these methods, the series method introduced by Kravchenko and Liberman give the most accurate results for the low-lying spectra of hydrogen atom in a magnetic field [16－18]. The disadvantage of this method is its requirement

for high computational precision up to 280 decimal digits, which is not available in common computers [16]. This drawback limits its application. In the calculation for high-lying excited states of Rydberg hydrogen atoms in an experimental available magnetic field, basis set method using Sturmian basis [19] and adiabatic coupling channels method are widely used ones [20, 21].

In the calculation of atoms in a strong magnetic field, the choice of coordinates play an important role in simplifying calculations. In general, when Coulomb interaction is much larger than the diamagnetic term, spherical coordinates is appropriate; otherwise, cylindrical coordinates should be adopted. If Coulomb interaction is comparable to diamagnetic interaction, there is no optimal choice of coordinates. We would mention that semi-paraboloidal coordinates are often adopted in studying statistical the characteristics of high-lying diamagnetic spectra of atoms [22]. It is noted that the Hamiltonian of a hydrogen atom in the field-free case is all separable in spherical, paraboloidal and spheroidal coordinates. The former two coordinates are widely used in the problem of a hydrogen atom in an external field, while the latter is scarcely applied for this problem. It is well known that the classical counterpart of the hydrogen atom problem is a Kepler problem that the orbit of a planet is an ellipse. Furthermore, the ground electron cloud of free hydrogen atom is spherically symmetrical, which turn to "spheroidal" symmetrical in a magnetic field due to the diamagnetic interaction. In addition, spheroidal coordinates is the bridge connected with spherical and paraboloidal coordinates, which turns to spherical coordinates as the foci is close to zero and turns to paraboloidal coordinates as the foci is close to infinity. Based on the consideration above, it is predicted that the calculation efforts should be reduced by choosing an appropriate foci in spheroidal coordinates. Thus, to calculate the ground and low excited states for the hydrogen atom in a strong magnetic field or high Rydberg hydrogen atom in an experimental magnetic field, spheroidal coordinates would be a good choice.

In this paper, we would make an attempt to calculate the energy spectra for hydrogen in a strong magnetic field in the framework of spheroidal coordinates. B-splines basis set method is used. The validity and efficiency of the methods are confirmed by comparing with previous accurate results. The advantage of the method is discussed in brief.

2 Theory and method

In this paper, we apply spheroidal coordinates (u, v, ϕ) to calculate the energy of hydrogen atom in a strong magnetic field. Here, the variables u and v are defined as $u = (r_1 + r_2)/2f$ and $v = (r_1 - r_2)/2f$ with r_1 and r_2 being the distances of electron from two foci, respectively. In these coordinates, the Hamiltonian can be written as (atomic units are used throughout this paper):

$$H = H_0 + V_{\text{coul}} + \frac{\gamma}{2}\mathrm{i}\frac{\partial}{\partial\phi} + \frac{1}{8}\gamma^2 f^2 (u^2-1)(1-v^2) \tag{1}$$

where H_0 is the kinetic energy operator as

$$H_0 = -\frac{1}{2}\frac{1}{f^2(u^2-v^2)}\left[\frac{\partial}{\partial u}(u^2-1)\frac{\partial}{\partial u} + \frac{\partial}{\partial v}(1-v^2)\frac{\partial}{\partial v} + \frac{u^2-v^2}{(u^2-1)(1-v^2)}\frac{\partial^2}{\partial\phi^2}\right] \tag{2}$$

$V_{\text{coul}} = -1/f(u + v)$ is the electron-nucleus Coulomb potential. The third and forth terms in the right of Eq. (1) are paramagnetic and diamagnetic potential with γ being strength of magnetic field in atomic unit (1 a.u. = 2.35×10^5 T). Since Hamiltonian is invariable to rotation about the z-axis (symmetric axis), the quantum number (m) of the z-component of angular momentum is a good quantum number. For a given m, the wave functions can be factorized as:

$$\Psi(u,v,\phi) = \Phi(u,v)\frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}m\phi} \tag{3}$$

We expand $\Phi(u, v)$ as

$$\Psi(u,v) = \sum_{i,j} C_{ij}(u^2-1)^{\frac{|m|}{2}} B_{i,k}(u)(1-v^2)^{\frac{|m|}{2}} B_{j,k}(v) \tag{4}$$

where $B_{i,k}(u)$ and $B_{j,k}(v)$ are B-splines of order k defined at the interval [1, $u_{\max}$] and [−1, 1], respectively. $u_{\max}$ is a truncated radius determined by the distribution region of quantum states. The factors $(u^2-1)^{\frac{|m|}{2}}$ and $(1-v^2)^{\frac{|m|}{2}}$ are introduced to describe correctly the asymptotic behaviors in the field-free case for $u \to 1$ and $v \to \pm 1$. Meanwhile, it can remove the singularity in Eq. (2) so as to ensure the stability of numerical calculation. B-splines are piece-polynomials determined uniquely by the knot sequence and the order k. Due to its multiple advantages, such as high localization, quickness and accuracy in the calculation of matrix elements, numerical stability, and famous flexibility, B-splines are widely applied in atom and molecular physics in the last decade. For some details of the characteristics of B-splines and their application, the reader can refer to the literatures [23—27]. In the function space spanned by B-spline-type basis [see Eq. (4)], the Schrödinger equation can be written in a matrix form:

$$HC = ESC \tag{5}$$

where E is the eigenenergy and C the corresponding eigenvector, H and S are the Hamiltonian and overlap matrix, respectively. The energy eigenvalues and the corresponding eigenstates can be obtained by diagonalizing the Hamiltonian. The high localization of B-splines results in banded matrix H and S, which speeds up the computation and reduces considerably the memory requirement.

3 Results and discussions

With the method introduced in the previous section, we have

calculated low-lying energies of hydrogen in a strong magnetic field with strength region being [0, 1000 a.u.]. In the calculation, the order of B-splines $k = 7$ is assumed. The B-spline knots in u direction is distributed exponentially in the intervals [1, u_{max}], while the B-spline knots in v direction are distributed uniformly in the intervals [−1, 1]. The truncated radius $u_{max} = 30$ a.u. is adopted, which is big enough for the calculation of low-lying states. The foci f is introduced as a non-linear variational parameter. This makes the proposed method more flexible and reduces the size of basis set considerably.

Our results for the lowest energies of $m = 0$ ($1s_0$) and $m = -1$ ($2p_{-1}$) states are shown in Table 1 and Table 2, respectively. All the data are convergent to the last digit. In Table 1, we also show the dimension of bases and the optimized foci R. The most accurate results given by Kravchenko and Liberman [16] and by Dimova *et al*. [15] are presented for comparison. For $1s_0$ state, our results have 12 significant figures for $\gamma \leqslant 100$ a.u. and 11 significant figures for $\gamma =$ 1000 a.u., respectively. For $2p_{-1}$ state, 11 significant figures for $\gamma \leqslant 100$ a.u. and 9 significant figures for $\gamma = 1000$ a.u. are obtained. In the case of lower magnetic field ($\gamma \leqslant 10$ a.u.), our results have the same accuracy as the results by Kravchenko and Liberman [16], the most accurate results up to date. In all the strength region considered in this paper, our results are superior to that of Dimova *et al*. [15].

From Table 1 and Table 2, we can also see that with the increasing of the magnetic field, it is necessary to increase the dimension of bases both u direction and v direction in order to ensure high accurate results. In addition, the optimized foci decrease with the increasing of the magnetic field and the optimized foci for excited state are greater than those for the ground state. Although the dimension of bases reach 8400 for the case of $\gamma = 1000$ a.u., the diagonalization of such a large matrix can be quickly carried out in a PC machine due to the banded property of Hamiltonian matrix resulting from the localization characteristic of B-splines.

Table 3 shows a comparison for ground energy of hydrogen atom in magnetic fields obtained by adopting three different coordinates. B-spline basis sets are adopted in all three calculations. The results using cylindrical coordinates are performed by Wang and Hsue [7]. We re-carried out a calculations using the method introduced by Xi *et al*. [6] who calculate the hydrogen atom in magnetic field adopting spherical coordinates. To facilitate the comparison, the same size of basis sets are adopted in both spherical and spheroidal coordinates (the size of basis set for different magnetic fields see Table 1). From Table 3, in all the field strengths under consideration, we can see that the results obtained by using spheroidal coordinates are more close to the accurate values given by Kravchenko and Liberman [16] than those by using spherical and cylindrical coordinates. For stronger magnetic field, such as $\gamma = 1000$ a.u., the results by sphroidal coordinates have 11 significant figures, while those by spherical coordinates have only 4 significant figures. This indicates that spherical coordinates is not suitable when magnetic field $\gamma > 100$ a.u.. In the high field region, cylindrical coordinates is prefer to spherical one. It is evident that spheroidal coordinates would be a good candidate in the calculation of the hydrogen atom in strong magnetic fields.

Table 1 The total energy $1s_0$ state of hydrogen atom for different magnetic field, where N_u and N_v are the dimension of bases used in u- and v-direction, respectively. $R = 2f$ is the optimized variational parameter. In the last column, the numbers in brackets denote the possible uncertainties in significant figure given by the authors of Ref. [15].

γ/a.u.	$N_u \times N_v$	R	E_0	Ref. [16]	Ref. [15]
0	20×30	1.292	−0.499 999 999 998		−0.500 000 000 00 (2)
1	30×40	1.218	−0.331 168 896 734	−0.331 168 896 733	
10	50×70	0.567	3.252 202 836 28	3.252 202 836 286	3.252 202 836 (46)
100	70×90	0.385	46.210 195 763 697	46.210 195 736 697	46.210 195 764 (66)
1000	60×140	0.236	492.337 576 77	492.337 576 752 245	492.337 577 098 (80)

Table 2 The same as Table 1 but for $2p_{-1}$ state.

γ/a. u.	$N_u \times N_v$	R	$E_{2p_{-1}}$	Ref. [15]
0.0001	20×30	2.833	−0.124 999 969 99	−0.124 999 97
1	30×40	1.362	0.543 402 941 57 8	0.543 402 941 576
10	50×70	0.899	8.874 577 658 16	8.874 577 658 16
100	70×90	0.412	97.365 239 339	97.365 239 334 701
1000	60×140	0.230	994.361 579 8	994.361 578 92

Table 3 Comparison for the ground of hydrogen atom in magnetic field obtained in different coordinates. B-spline basis sets are adopted in all three calculations.

γ/a.u.	Cylindrical coordinates [7]	Spherical coordinates [6]	Spheroidal coordinates
0	−0.500 000 000 00	−0.499 999 999 998	−0.499 999 999 999
0.0001		−0.499 999 996 5	−0.499 999 997 49
1	−0.331 168 892 5	−0.311 168 896 734	−0.331 168 896 73
10	3.252 202 852 45	3.252 202 836 3	3.252 202 836 28
100	46.210 196 027 85	46.210 195 8	46.210 195 763 7
1000	492.337 580 93	492.824	492.337 576 77

Table 4 Comparison for the energy spectra of hydrogen atom in a magnetic field (B = 4.7 T) between present results and those of Clark and Taylor [19]. The energy spectra is near the principal quantum number n = 23.

m = 0		m = 1		m = 2		Parity
Present work	Clark	Present work	Clark	Present work	Clark	
–0.943 867 373 2	–0.943 867 4	–0.932 659 577 9	–0.932 659 6	–0.921 557 224 2	–0.921 557 2	even
–0.943 867 373 1	–0.943 867 4	–0.932 659 576 1	–0.932 659 6	–0.921 557 188 1		odd
–0.941 515 880 9	–0.941 515 9	–0.930 486 774 9	–0.930 486 8	–0.919 581 440 2	–0.919 581 4	even
–0.941 515 814 1	–0.941 515 8	–0.930 485 663 8	–0.930 485 7	–0.919 570 7421 1		odd
–0.939 552 070 6	–0.939 552 1	–0.928 797 580 7	–0.928 797 6	–0.918 249 544 1	–0.918 249 5	even
–0.939 537 548 2	–0.939 537 5	–0.928 700 635 8	–0.928 700 6	–0.917 928 871 2		odd
–0.938 249 658 6	–0.938 249 7	–0.927 740 452 4	–0.927 740 5	–0.917 063 119 7	–0.917 063 1	even
–0.937 891 070 3	–0.937 891 1	–0.927 057 449 0	–0.927 057 4	–0.916 153 652 6		odd
–0.937 016 829 0	–0.937 016 8	–0.926 099 512 8	–0.926 099 5	–0.915 076 765 1	–0.915 076 8	even
–0.936 085 474 7	–0.936 085 5	–0.925 015 079 4	–0.925 015 1	–0.913 867 765 4		odd
–0.934 994 113 8	–0.934 994 1	–0.923 796 664 6	–0.923 796 7	–0.912 530 662 6	–0.912 530 7	even
–0.933 772 924 1	–0.933 772 9	–0.922 451 955 0	–0.922 452 0	–0.911 069 137 1		odd
–0.932 425 680 6	–0.932 425 7	–0.920 984 006 5	–0.920 984 0	–0.909 485 325 1	–0.909 485 3	even
–0.930 955 604 7	–0.930 955 6	–0.919 394 734 8	–0.919 394 7	–0.907 780 586 9		odd
–0.929 364 521 5	–0.929 364 5	–0.917 685 318 3	–0.917 685 3	–0.905 955 794 7	–0.905 955 8	even
–0.927 653 551 0	–0.927 653 6	–0.915 856 487 1	–0.915 856 5	–0.904 011 498 9		odd
–0.925 823 377 1	–0.925 823 4	–0.913 908 679 2	–0.913 908 7	–0.901 948 027 8	–0.901 948 0	even
–0.923 874 400 6	–0.923 874 4	–0.911 842 132 4	–0.911 842 1	–0.899 765 550 0		odd
–0.921 806 830 1	–0.921 806 8	–0.909 656 943 0	–0.909 656 9	–0.897 464 116 2	–0.897 464 1	even
–0.919 620 737 6	–0.919 620 7	–0.907 353 102 3	–0.907 353 1	–0.895 043 686 5		odd
–0.917 316 095 2	–0.917 316 1	–0.904 930 522 3	–0.904 930 5	–0.892 504 150 0	–0.892 504 2	even
–0.914 892 798 8	–0.914 892 8	–0.902 389 052 6	–0.902 389 1			odd
–0.912 350 684 9	–0.912 350 7					even

In the last two decades, there has been a large number of studies on the characteristics of diamagnetic spectra of the Rydberg hydrogen atom for its important in understanding the correspondence between quantum and classical systems. One of the important works in this field is the accurate calculation of the diamagnetic spectra of the hydrogen atom. Clark and Taylor are the first to carry out such a calculation using Sturmian basis set method [19]. In order to verify the feasibility of the proposed method in the calculation of high excited states. we have carried out a calculation of diamagnetic spectra of a Rydberg hydrogen atom. We show the comparison for the energy spectra of hydrogen atom in magnetic field between our results and Clark and Taylor [19] in Table 4, where the main quantum number n = 23 and magnetic field is 4.7 T (these energy spectra are just entered into the n mixed region). In our calculation, the dimension of bases is $N_u \times N_v = 100 \times 50$ and the truncated radius $u_{\max}$ = 4000 a.u.. From Table 4, it is obvious that our results are completely accordant with theirs. Our results are accurate to 10 significant figures. For the calculation of energy spectra and the oscillator strength spectra in the strong n mixed region, the proposed method can also give a high accuracy results, relevant results will appear elsewhere.

4 Conclusions

In this paper we have introduced a feasible method to calculate the energy spectra for hydrogen in a strong magnetic field in the framework of spheroidal coordinates; B-spline functions has been used as basis set. The proposed method is not only valid to calculate low-lying energy spectra for hydrogen in a strong magnetic field, but also valid to calculate high-excited energy spectra with high accuracy for Rydberg atoms in an experimental magnetic field. Adopting spheroidal coordinates, the dimension of bases could be effectively reduced by adjusting the foci position. Due to the high localization of B-splines, with which the Hamiltonian matrix result in a banded one, the memory requirement and the computation time are reduced considerably, and then the large basis set expansion could be realized in PC. The proposed method is appropriate to calculate the energy spectra for hydrogen in an arbitrary magnetic field and high Rydberg hydrogen atoms with high speed and high accuracy. It is known that the problem hydrogen atom in an electric field is separable in paraboloidal coordinates. It is expected that the proposed method would be feasible for use on hydrogen atom in parallel and crossed magnetic and electric

fields. Such a study is underway.

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