Highly Accurate Solution for a Hydrogen Atom in a Uniform Magnetic Field

Yu. P. Kravchenko,[1,2] M. A. Liberman,[1,2] and B. Johansson[1]
[1]*Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden*
[2]*P. Kapitsa Institute for Physical Problems, Russian Academy of Sciences, Vorob'evskoe sh. 2, Moscow, 117334, Russia*
(Received 19 January 1996)

The highly accurate series solution for a hydrogen atom in a uniform magnetic field of arbitrary strength is obtained. It is derived in the form of a power series in two variables, the radius and the sine of the cone angle, with explicit recurrent relations for the coefficients of the power series. As an illustration, a brief list of energy values with accuracy 10^{-12} hartree for the magnetic field $0 < B/(m_e^2 e^3 c/\hbar^3) \leq 4000$ and pictures of selected anticrossings in the chaotic region of the spectrum are presented. [S0031-9007(96)00716-8]

PACS numbers: 32.60.+i, 02.30.Jr, 03.65.Ge, 97.60.Jd

The problem of the hydrogen atom in a uniform magnetic field attracts attention of physicists from the early days of quantum mechanics. The interest in this problem is caused by numerous occurrences of the quadratic Zeeman effect in astronomy and astrophysics [1–3], solid state physics [4–6], atomic spectroscopy [7], and investigations of quantum chaos [8,9].

It is well known that the magnetic field completely destroys the supersymmetry of the field-free Coulomb problem, making the separation of variables impossible. In the low-field regime the problem can be treated by the usual perturbation theory methods. The behavior of the spectrum in this region is essentially defined by the existence of the approximate symmetry of the problem [8,10,11]. In the opposite limit of extremely strong magnetic field the solution is substantially facilitated by using the adiabatic approximation [4,12]. However, in the intermediate region, where the magnetic and Coulomb interactions are comparable, the problem is extremely complicated. Each step towards the better understanding of the problem was always accompanied by immense difficulties. The problem was treated by numerous methods, including variational methods [13–15], eigenvalue analysis [12,16–18], semianalytical methods [19], the dimensional perturbation theory [20], and fully numerical methods, including the Hartree-Fock-like schemes [21] and the finite element method [22].

In this paper we present a new approach to the problem, which, in particular, provides solution in the intermediate region of the magnetic field strength with any desirable accuracy. We consider the nonrelativistic formulation and derive a rigorous series expansion of the wave function in the one-body approximation. The wave function is given by a double series in two variables, the radius and the sine of the cone angle. All nondiagonal terms of the series are explicitly expressed via recurrent relations, and diagonal terms are linked to the boundary condition at infinity. The solution of the problem is thus reduced to the solution of a truncated system of algebraic equations. Since the knowledge of the analytical structure of the series allows efficient calculation of solution with very high numerical precision, the obtained solution is in a sense equivalent to ordinary special functions.

In order to illustrate the obtained solution we present energy values calculated with precision 10^{-12} hartree for the low-lying states in the magnetic field range up to 10^{13} G and for highly excited states in the chaotic regime. The precision of the reported results is better than that of most of the calculations published before and proves applicability of our solution to all field strengths and, in particular, to the chaotic region.

It is well known that for fields below 10^{13} G relativistic corrections are negligible [14], and the spin-orbit coupling is small if $Bn^3 > 10^5$ G [23]; the motion of the nucleus can be accounted for by a constant shift in energy [24]. Therefore, we consider the one-body problem in the nonrelativistic approximation. Introducing the spherical system of coordinates (r, θ, φ) with the axis along the field $\mathbf{H} = (H\cos\theta, -H\sin\theta, 0)$, taking $\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r} = (0, 0, \frac{1}{2}Hr\sin\theta)$, and choosing the atomic system of units $\hbar = m_e = e = 1$, we present the total wave function as

$$\Psi(r, \theta, \varphi) = e^{im\varphi}(r\sin\theta)^{|m|}(r\cos\theta)^{\nu}\psi(r, \theta), \qquad (1)$$

where m is the magnetic quantum number and ν is the z parity. The Schrödinger equation becomes

$$\psi_{rr} + 2\frac{|m| + \nu + 1}{r}\psi_r + \frac{1}{r^2}\psi_{\theta\theta} + \frac{1}{r^2}[(2|m| + 1)\cot\theta - 2\nu\tan\theta]\psi_\theta = \left[\frac{1}{4}\gamma^2 r^2\sin^2\theta - \frac{2}{r} - (1 + |m|)\gamma + 2E_b\right]\psi . \qquad (2)$$

The total energy is expressed via the parameter $E_b = (1 + m + |m|)\gamma/2 - E$, coinciding with the binding energy $\mathcal{E} = \gamma/2 - E$ for $m \leq 0$, and the magnetic field is given by $\gamma = H/H_0$, $H_0 = m_e^2 e^3 c/\hbar^3 = 2.35 \times 10^9$ G.

We look for the solution of Eq. (2) in the form of a power series in r with coefficients which depend on $t = \sin\theta$, $\psi(r,\theta) = \sum_{i=0}^{\infty} f_i(t) r^i$. Substituting this expansion into the Schrödinger equation (2), we obtain [if $n < 0$, then by definition $f_n(t) \equiv 0$]

$$(1 - t^2) f_i'' + \frac{2|m| + 1}{t} f_i' - 2(|m| + \nu + 1) t f_i' + i(i + 2|m| + 2\nu + 1) f_i = \frac{1}{4}\gamma^2 t^2 f_{i-4} + \varepsilon f_{i-2} - 2 f_{i-1}, \quad (3)$$

where $\varepsilon = 2E_b - (|m| + 1)\gamma$. This equation is a nonhomogeneous linear differential equation, and any solution of (3) may be presented as the sum of a particular integral, which we denote $G_i(t)$, and any complementary function $F_i(t)$. We start from the homogeneous equation corresponding to Eq. (3) and look for $F_i(t)$ in the form $F_i(t) = \sum_{j=0}^{\infty} b_{i,j} t^j$. Substituting this expression into the homogeneous equation, we obtain the following recurrent relation:

$$b_{i,j+2} = -\frac{(i - j)[i + j + 2(|m| + \nu) + 1]}{(j + 2)(j + 2|m| + 2)} b_{i,j}. \quad (4)$$

If $j \to \infty$, then $b_{i,j+2}/b_{i,j} = 1$, and $F_i(1) = \infty$ unless the series $F_i(t)$ terminates at a finite j. It happens for $j = i$ and means that if i is even then $b_{i,0} = C_i$, $b_{i,1} = 0$, and if i is odd then $b_{i,0} = 0$, $b_{i,1} = C_i$. In both cases $F_i(t)$ is the product of an unknown constant C_i by a polynomial of degree i with the lowest coefficient equal to unity, which we designate as $H_i(t) = \sum_{j=0}^{i} h_{i,j} t^j$.

We seek the particular integral of the nonhomogeneous equation (3) in the form $G_i(t) = \sum_{j=0}^{\infty} a_{i,j} t^j$. It can be rigorously proven that $G_i(t)$ is also a polynomial of degree i, whose coefficients are given by the recurrent relation

$$(i - j)(i + j + 2|m| + 2\nu + 1) a_{i,j} + (j + 2)(j + 2|m| + 2) a_{i,j+2} = \frac{1}{4}\gamma^2 d_{i-4,j-2} + \varepsilon d_{i-2,j} - 2 d_{i-1,j}, \quad (5)$$

where $d_{i,j} = a_{i,j} + C_{i,j} h_{i,j}$ and $a_{i,i}$ can be taken as zeros (if $i < 0$ or $j < 0$, then $a_{i,j} = 0$ and $h_{i,j} = 0$). Since the function $\psi(r,\theta)$ obeys the boundary condition on the axis $\partial\psi(r,\theta)/\partial\theta|_{\theta=0} = 0$, all the coefficients $a_{i,j}$ and $b_{i,j}$ with odd j are also zeros. The final structure of solution is the following:

$$\psi(r,\theta) = \sum_{k=0}^{\infty} \sin^{2k}\theta \sum_{i=2k}^{\infty} A_{i,2k} r^i, \quad (6)$$

$$A_{i,2k} = \begin{cases} a_{i,2k} + C_i h_{i,2k}, & i = 2p, \\ a_{i,2k}, & i = 2p + 1. \end{cases} \quad (7)$$

Here $\{C_{2p}\}$ are unknown coefficients, $h_{i,0} = 1$,

$$h_{i,2k+2} = -\frac{(i - 2k)[i + 2k + 2(|m| + \nu) + 1]}{4(k + 1)(k + |m| + 1)} h_{i,2k}, \quad (8)$$

$a_{i,2k} = 0$ if $2k \geq i$, and $a_{i,2k}$ for $2k < i$ are given by Eq. (5) with j replaced by $2k$. The solution is completely determined by the infinite set of coefficients $\{C_{2p}\}$ and the eigenvalue E_b. Since the Schrödinger equation is homogeneous, one of the coefficients can be taken arbitrarily.

In order to obtain boundary conditions we rewrite the series (6) in the form

$$\psi(r,\theta) = \sum_{k=0}^{\infty} \gamma^k (r\sin\theta)^{2k} g_{2k}(r), \quad (9)$$

where $g_{2k}(r) = \gamma^{-k} \sum_{i=2k}^{\infty} A_{i,2k} r^{i-2k}$. Substitution of (9) into Eq. (2) gives the following chain of equations:

$$g_{2k}'' + \frac{2}{r}(2k + |m| + \nu + 1) g_{2k}' + \left(\frac{2}{r} - \varepsilon\right) g_{2k} = \frac{\gamma}{4} g_{2k-2} - 4\gamma(k + 1)(k + |m| + 1) g_{2k+2}. \quad (10)$$

For any nonzero intensity of the field the asymptotic behavior of $g_0(r)$ is given by [4]

$$g_0(r) \sim r^{1/\kappa} \exp(-\kappa r), \qquad \kappa = \sqrt{2E_b}. \quad (11)$$

Using Eq. (10), it can be proven that the same law describes the asymptotic behavior of any function $g_{2k}(r)$. Therefore, the boundary condition at infinity is

$$\lim_{r\to\infty} \frac{g_{2k}'(r)}{g_{2k}(r)} = -\kappa, \qquad k = 0, \ldots, \infty. \quad (12)$$

The obtained set of boundary conditions is equivalent to the set of unknowns and is sufficient for the solution of the problem.

To obtain quantitative results, we must reduce infinite parameters to finite values. First, we introduce a reduced solution $\Phi_R(r,t)$, which joins the asymptote at a finite radius R,

$$g_{2k}'(R) + \kappa g_{2k}(R) = 0, \quad (13)$$

the index k goes from 0 to ∞. The exact wave function is given by $\psi(r,t) = \lim_{R\to\infty} \Phi_R(r,t)$.

Second, we must truncate the infinite set of coefficients $\{C_{2p}\}$ at a finite cutoff index, say l, such that the solution satisfies only a finite set of conditions (13). This operation can be performed in two different ways: either we put to zero all C_{2p} with $p > l$ or we put to zero radial functions g_{2k} with $k > l$. In terms of coefficients C_{2p} the second method means that C_{2p} with $p > l$ are determined by the requirement $a_{2p,2l+2} + C_{2p} h_{2p,2l+2} = 0$. The second

TABLE I. Binding energies (atomic units) of the ground state for various values of the field and of several excited states for $\gamma = 1$ (uncertainty is ± 1 in the last digit). The third column shows corresponding R and l.

γ	E_b (ground state)	R/l	State	E_b ($\gamma = 1$)	R/l
1	0.831 168 896 733	20./20	$2s_0$	0.160 468 982 634	43./24
10	1.747 797 163 714	13./21	$2p_0$	0.260 006 615 944	39./22
100	3.789 804 2363 05	8.4/24	$2p_{-1}$	0.456 597 058 424	25./25
200	4.727 145 110 687	6.5/25	$3d_0'$	0.066 233 066 419	130./18
500	6.257 087 674 681	5.2/25	$3p_0$	0.090 224 511 338	78./18
1000	7.662 423 247 755	5.2/25	$3d_{-1}$	0.206 567 363 860	39./20
2000	9.304 765 082 770	4.4/25	$3d_{-2}$	0.353 048 025 149	33./22
4000	11.204 145 206 603	3.9/26	$4f_{-3}$	0.299 968 970 495	34./23

scheme strongly reduces computational effort, because now we do not have to calculate $a_{i,2k}$ and $h_{i,2k}$ with $k > l$.

In both cases we have $l + 1$ unknown coefficients C_{2p}, $p = 0, \ldots, l$, but due to the homogeneity of Eq. (2) one of them may be taken arbitrarily, e.g., $C_0 = 1$. Hence, we have only $l + 1$ unknowns, l coefficients C_{2p}, and energy E_b. The truncated solution is required to satisfy $l + 1$ boundary conditions (13) with k running from 0 to l.

Let us take an index q, $0 \le q \le l$, and put $C_{2p} = 0$ for $p \ne q$ and $C_{2q} = 1$. If we now compute all $A_{i,2k}$ according to (7) (we shall label them $A^q_{i,2k}$), then instead of true radial functions $g_{2k}(r)$ we obtain functions $w^q_{2k}(r) = \gamma^{-k} \sum_{i=2k}^{\infty} A^q_{i,2k}\, r^{i-2k}$. Since Eq. (5) is linear, $g_{2k}(r) = \sum_{q=0}^{l} C_{2q} w^q_{2k}(r)$, and boundary conditions take the form ($k = 0, \ldots, l$)

$$\sum_{q=0}^{l} C_{2q} w^{q\prime}_{2k}(R) + \kappa \sum_{q=0}^{l} C_{2q} w^{q}_{2k}(R) = 0 . \qquad (14)$$

Summation over i can be performed numerically, because in both methods terms $A_{i,2k} r^i$ decay rapidly when $i \to \infty$; typically it must be extended to $i \sim 10^2$–10^3.

We can directly solve the system (14), $k = 1, \ldots, l$, with respect to the l unknown coefficients C_{2p}. The resulting left-hand part of (14) at $k = 0$, which we designate as $\Delta(E_b)$, nonlinearly depends on E_b and in general differs from zero. Roots of the equation $\Delta(E_b) = 0$ give the energy levels in the taken l, R approximation. These roots can be found by an iterative method with any desired precision.

As the cutoff index l increases, the solution converges to its limiting function $\Phi_R(r, t)$. The energy levels in the l, R approximation converge to the values in R approximation: $\lim_{l\to\infty}(E_b)_{l,R} = (E_b)_R$. Computations show that the difference $|(E_b)_{l+1,R} - (E_b)_{l,R}|$ exponentially decreases with l, making it possible to determine the upper bound to the error introduced by a finite l.

Both methods give the energy levels $(E_b)_R$ and wave functions $\Phi_R(r, t)$ in the R approximation. For a good approximation to the exact solution the value of R must be, at least, larger than the distance from the nucleus to the farthest extremum of the wave function. Numerical calculations show that, if this condition is satisfied, the convergence of solution with the increasing of R is rather fast: for a given δR the difference $|(E_b)_{R+\delta R} - (E_b)_R|$ decreases with R exponentially. This fact allows us to obtain an upper bound to the error of approximation and to control the accuracy of the results.

Convergence of the described scheme can be substantially accelerated by introducing an additional multiplier $\exp(-\frac{1}{4}\gamma r^2 \sin^2\theta)$ into the right-hand side of Eq. (1). The whole procedure described above remains applicable without any modifications, except that the right-hand side of Eq. (5) comprises a different sum of coefficients. The combination of this scheme with the second method of truncation allows one to compute energy levels evolving from the field-free states $n < 10$ with accuracy 10^{-10} hartree using typically $l = 20, \ldots, 30$.

The above algorithm allows a very efficient tabulation of energies and wave functions with very high accuracy. Calculation of the ground state energy for $\gamma = 1$ with precision 10^{-6} hartree takes only a few seconds with a usual personal computer. In Table I we give, as an illustration, a short list of binding energies with precision 10^{-12} hartree. Extensive accurate tables will be published elsewhere.

Energy levels for highly excited states up to principal quantum number $n = 10$ are shown on Fig. 1. Since the developed method allows one to obtain the solution with

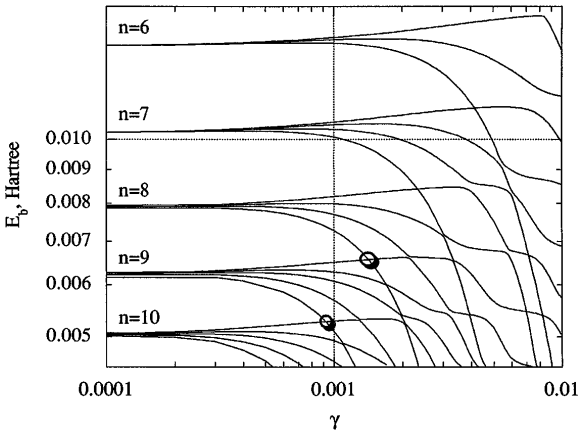

FIG. 1. Binding energy of hydrogen as a function of magnetic field for several states in the intermediate regime ($m = 0$, $\nu = +1$).

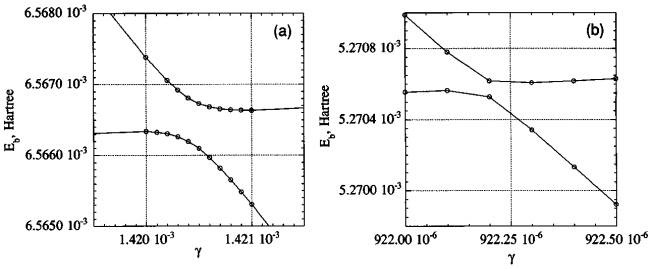

FIG. 2. Pictures of the first anticrossings between levels with $m = 0$, $\nu = +1$, and (a) $n = 8$ and $n = 9$; (b) $n = 9$ and $n = 10$.

very high numerical precision, it is possible to resolve anticrossings of any terms. As an example, this is illustrated by Figs. 2(a) and 2(b) for the first anticrossings between levels with principle quantum numbers 8, 9, and 9, 10, where the repulsion between levels becomes 6×10^{-7} and 9×10^{-8} hartree, respectively. Our results show that repulsion of first anticrossings between levels with adjacent principal quantum numbers exponentially decreases with the increase of n [8].

Since our approach to the problem employs the analytical structure of the wave function, it is free of several limitations inherent to approximate methods. First of all, the obtained solution works throughout the whole range of magnetic field strength including the intermediate region, which is characterized by sharp changes in the localization of the wave functions and through which until now only a limited number of excited states was traced. Second, the character of convergence guarantees the precision of results, which is especially important for excited states in the intermediate region, where no eigenvalue technique for establishing lower and upper bounds has been reported.

This work was supported by the Swedish Natural Research Council (NFR), Contract No. F-AA/FU 10297-307, and by the Swedish Royal Academy, Contract No. 1482.

[1] R. H. Garstang and S. B. Kemic, Astrophys. Space Sci. **31**, 103 (1974).
[2] R. Östreicher *et al.*, Astron. Astrophys. **257**, 353 (1992).
[3] A. Yu. Potekhin and G. G. Pavlov, Astrophys. J. **407**, 330 (1993).
[4] R. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 196 (1960).
[5] S. M. Dickmann and D. I. Sidel'nikov, Phys. Lett. A **187**, 79 (1994), and references therein.
[6] A. V. Korolev and M. A. Liberman, Phys. Rev. B **47**, 14 318 (1993); **50**, 14 077 (1994); Phys. Rev. Lett. **72**, 270 (1994).
[7] P. Cacciani, E. Luc-Koenig, J. Pinard, C. Thomas, and S. Liberman, Phys. Rev. Lett. **56**, 1124 (1986).
[8] H. Friedrich and D. Wintgen, Phys. Rep. **183**, 37 (1989), and references therein.
[9] J. Zakrzewski, K. Dupret, and D. Delande, Phys. Rev. Lett. **74**, 522 (1995).
[10] E. A. Solov'ev, JETP Lett. **34**, 265 (1981).
[11] M. L. Zimmerman, M. M. Kash, and D. Kleppner, Phys. Rev. Lett. **45**, 1092 (1980).
[12] C.-R. Liu and A. F. Starace, Phys. Rev. A **35**, 647 (1987).
[13] J. A. C. Gallas, J. Phys. B **18**, 2199 (1985).
[14] S. P. Goldman and Z. Chen, Phys. Rev. Lett. **67**, 1403 (1991); Z. Chen and S. P. Goldman, Phys. Rev. A **44**, 4459 (1991); **45**, 1722 (1992); **48**, 1107 (1993).
[15] U. Kappes and P. Schmelcher, J. Chem. Phys. **100**, 2878 (1994).
[16] C. R. Handy, D. Bessis, G. Sigismondi, and T. D. Morley, Phys. Rev. Lett. **60**, 253 (1988).
[17] P. Falsaperla and G. Fonte, Phys. Rev. A **50**, 3051 (1994), and references therein.
[18] Z. Chen, G. Fonte, and S. P. Goldman, Phys. Rev. A **50**, 3838 (1994).
[19] O. L. Silva Filho and A. L. A. Fonseca, Phys. Rev. A **50**, 4383 (1994).
[20] T. C. Germann, D. R. Herschbach, M. Dunn, and D. K. Watson, Phys. Rev. Lett. **74**, 658 (1995), and references therein.
[21] H. Ruder, G. Wunner, H. Herold, and F. Geyer, *Atoms in Strong Magnetic Fields* (Springer-Verlag, Berlin, 1994).
[22] J. Shertzer, L. R. Ram-Mohan, and D. Dossa, Phys. Rev. A **40**, 4777 (1989).
[23] R. H. Garstang, Rep. Prog. Phys. **40**, 105 (1977).
[24] D. Baye and M. Vincke, Phys. Rev. A **42**, 391 (1990), and references therein.