LETTER TO THE EDITOR

Zeeman diamagnetism in hydrogen at arbitrary field strengths

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Abstract. The non-relativistic energy spectrum of the ground state of hydrogen-like atoms in magnetic fields of arbitrary strength is investigated by using variational functions. We present four- and five-parameter functions which produce energies almost as good as the best ones available in the literature.

In a recent article (Gallas 1985; hereafter to be referred to as I) it was proposed that a convenient basis for studying properties of hydrogenic systems in the presence of strong magnetic fields (i.e. the quadratic Zeeman effect) is one formed with functions of the generic type

$$\psi(\xi, \eta, \varphi) = \mathcal{N} \exp(\pm im\varphi) f(\xi, \eta) \exp[-\tfrac{1}{2}(a\xi + b\eta + c\xi\eta)] \tag{1}$$

where ξ, η, φ are parabolic coordinates, $f(\xi, \eta) = \sum_{ij=0}^{\infty} d_{ij}\xi^i \eta^j$ and a, b, c and d_{ij} are convenient variational parameters. The main advantages advocated for such a basis were that it is exact at both the Coulomb and Landau limits and that it allows all matrix elements needed in the calculations to be conveniently represented in terms of a single integral. Using $f(\xi, \eta) = 1$, the ground state of hydrogen was investigated in I where it was determined that, for that case, $a = b$. The motivation and difficulties in the study of the quadratic Zeeman effect (the 'last' unsolved problem of atomic physics) have been discussed recently in a number of review papers, for example by Kleppner *et al* (1983), Gay and Delande (1983) and Clark *et al* (1984).

The purpose of this letter is to report the results of an investigation of the convergence properties of the basis proposed in I. To this end, we will now study the ground state of hydrogen using as the trial function

$$\psi(\xi, \eta) = \pi^{-1/2} N f(\xi, \eta) \exp\{-\tfrac{1}{2}[a(\xi + \eta) + c\xi\eta]\} \tag{2a}$$

where

$$f(\xi, \eta) = 1 + p(\xi + \eta) + q\xi\eta + s(\xi^2 + \eta^2). \tag{2b}$$

Altogether this trial function contains five variational parameters: a, c, p, q and s. As we will see, (2) is able to produce remarkably accurate results that come very close to the best ones available in the literature.

Following I, the Hamiltonian of the problem is written as

$$H = -\tfrac{1}{2}\nabla^2 - Zr^{-1} + \tfrac{1}{8}\gamma^2(x^2 + y^2) \tag{3}$$

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and, correspondingly, the total energy is given by

$$E = \mathbb{K} + \mathbb{C} + \mathbb{Z} \tag{4a}$$

where

$$\mathbb{K} = -\tfrac{1}{2}\langle \nabla^2 \rangle \tag{4b}$$

$$\mathbb{C} = -Z\langle r^{-1} \rangle \tag{4c}$$

$$\mathbb{Z} = \tfrac{1}{8}\gamma^2 \langle x^2 + y^2 \rangle. \tag{4d}$$

As usual, the magnetic field strength γ is measured in units of 2.35×10^9 G. Now the energy can be expressed as a function of the variational parameters and of the integral

$$Y \equiv Y_1^1(a, a, c) = \int_0^\infty \frac{t \exp(-at)}{a + ct}\, dt$$

(see I for details). Writing

$$N^{-2} = u_0 + v_0 Y \tag{5a}$$

$$\mathbb{K} = N^2(u_1 + v_1 Y) \tag{5b}$$

$$\mathbb{C} = ZN^2(u_2 + v_2 Y) \tag{5c}$$

$$\mathbb{Z} = \tfrac{1}{8}\gamma^2 N^2(u_3 + v_3 Y) \tag{5d}$$

we find

$$u_0 = -\frac{2p^2}{a^3 c^2}(2a^2 - c) + \frac{2pq}{a^2 c^3}(2a^2 + 3c) + \frac{4ps}{a^4 c^3}(2a^4 + a^2 c + 3c^2) + \frac{4p}{a^2 c}$$

$$- \frac{q^2}{ac^4}(a^2 + 4c) - \frac{4qs}{a^3 c^4}(a^4 + 3a^2 c - c^2) - \frac{2q}{ac^2}$$

$$- \frac{4s^2}{a^5 c^4}(a^6 + 2a^4 c + a^2 c^2 - 6c^3) - \frac{4s}{a^3 c^2}(a^2 - c) \tag{6}$$

$$v_0 = \frac{2p^2}{c^2}(2a^2 + 3c) - \frac{2pq}{ac^3}(2a^4 + 7a^2 c + 2c^2) - \frac{4ps}{ac^3}(2a^4 + 5a^2 c + c^2)$$

$$- \frac{2p}{ac}(2a^2 + c) + \frac{q^2}{c^4}(a^4 + 6a^2 c + 6c^2) + \frac{4qs}{c^4}(a^4 + 5a^2 c + 3c^2)$$

$$+ \frac{2q}{c^2}(a^2 + 2c) + \frac{4s^2}{c^4}(a^4 + 4a^2 c + 3c^2) + \frac{4s}{c^2}(a^2 + c) + 1 \tag{7}$$

$$u_1 = \frac{p^2}{a^3} + \frac{2pq}{a^2 c} + \frac{6ps}{a^4} + \frac{p}{a^2} - \frac{q^2}{ac^2} - \frac{2qs}{ac^2} + \frac{4s^2}{a^5 c}(a^2 + 3c) + \frac{2s}{a^3} + \frac{1}{2a} \tag{8}$$

$$v_1 = p^2 - \frac{2pq}{ac}(a^2 + c) + \frac{2ps}{a} + \frac{q^2}{c^2}(a^2 + 2c) + \frac{2qs}{c^2}(a^2 + 2c) - \frac{4s^2}{c} - 2s \tag{9}$$

$$u_2 = -\frac{4p^2}{a^2 c} + \frac{4pq}{ac^2} + \frac{8ps}{a^3 c^2}(a^2 - c) - \frac{q^2}{a^2 c^3}(a^2 + 2c) - \frac{4qs}{a^2 c^3}(a^2 + c)$$

$$- \frac{2q}{a^2 c} - \frac{4s^2}{a^4 c^3}(a^4 + 3c^2) - \frac{4s}{a^2 c} - \frac{1}{a^2} \tag{10}$$

$$v_2 = \frac{2p^2}{ac}(2a^2+c) - \frac{4pq}{c^2}(a^2+2c) - \frac{8ps}{c^2}(a^2+c) - 4p + \frac{q^2}{ac^3}(a^4+4a^2c+2c^2)$$

$$+ \frac{4qsa}{c^3}(a^2+3c) + \frac{2q}{ac}(a^2+c) + \frac{4s^2}{ac^3}(a^4+2a^2c+c^2) + \frac{4sa}{c} + \frac{c}{a} \tag{11}$$

$$u_3 = -\frac{2p^2}{a^3c^4}(2a^4+7a^2c-c^2) + \frac{2pq}{a^2c^5}(2a^4+13a^2c+8c^2)$$

$$+ \frac{4ps}{a^4c^5}(2a^6+11a^4c+3a^2c^2+3c^3)$$

$$+ \frac{2p}{a^2c^3}(2a^2+3c) - \frac{q^2}{ac^6}(a^4+10a^2c+18c^2)$$

$$- \frac{4qs}{a^3c^6}(a^6+9a^4c+12a^2c^2-2c^3)$$

$$- \frac{2q}{ac^4}(a^2+4c) - \frac{4s^2}{a^5c^6}(a^8+8a^6c+9a^4c^2+2a^2c^3-6c^4)$$

$$- \frac{4s}{a^3c^4}(a^4+3a^2c-c^2) - \frac{1}{ac^2} \tag{12}$$

$$v_3 = \frac{2p^2}{c^4}(2a^4+11a^2c+9c^2) - \frac{2pq}{ac^5}(2a^6+17a^4c+30a^2c^2+6c^3)$$

$$- \frac{4ps}{ac^5}(2a^6+15a^4c+21a^2c^2+3c^3) - \frac{2p}{ac^3}(2a^4+7a^2c+2c^2)$$

$$+ \frac{q^2}{c^6}(a^6+12a^4c+36a^2c^2+24c^3) + \frac{4qs}{c^6}(a^6+11a^4c+28a^2c^2+12c^3)$$

$$+ \frac{2q}{c^4}(a^4+6a^2c+6c^2) + \frac{4s^2}{c^6}(a^6+10a^4c+23a^2c^2+12c^3)$$

$$+ \frac{4s}{c^4}(a^4+5a^2c+3c^2) + \frac{1}{c^2}(a^2+2c). \tag{13}$$

Table 1 shows the effect of various possible combinations of the variational parameters p, q and s on the energy. From this table one sees that by adding a variational parameter to the trial function one roughly obtains a further correct digit in the energies. By taking $q = 2s$ the trial function of $(2b)$ is reduced to

$$f(\xi, \eta) = 1 + p(\xi+\eta) + s(\xi+\eta)^2. \tag{14}$$

Table 1 shows that

$$f(\xi, \eta) = 1 + p(\xi+\eta) + q\xi\eta \tag{15}$$

produces much better results than (14). Note that $\xi+\eta$ is proportional to the radial distance between the particles $(r = (\xi+\eta)/2)$ while $\xi\eta = x^2+y^2$. Therefore the variational method favours linear terms in the variables appearing in the Hamiltonian (3).

In table 2 we compare some of the most accurate results for the binding energies available in the literature with those obtained from our equation (4) by minimising

Table 1. Effect of adding various parameters to the trial function when $\gamma = 1$ (corresponding to a magnetic field of 2.35×10^9 G). Energies are given in au.

Number of variational parameters	a	c	p	q	s	E	E_B
2	1.032 38	0.231 865	0	0	0	−0.329 558	0.829 56
	1.057 83	0.447 510	0	0.159 864	0	−0.330 523	0.830 52
3	1.341 00	0.201 546	0.211 539	0	0	−0.330 641	0.830 64
	0.971 72	0.236 659	0	0	−0.007 617	−0.330 715	0.830 72
	1.119 99	0.234 472	0.090 151	0	−0.011 302	−0.330 798	0.830 80
4	1.643 74	0.197 279	0.304 330	2s	0.068 535	−0.330 866	0.830 87
	0.995 71	0.427 285	0	0.119 866	−0.006 830	−0.330 875	0.830 88
	1.275 82	0.331 701	0.144 130	0.128 115	0	−0.331 122	0.831 12
5	1.449 55	0.286 066	0.215 446	0.160 118	0.023 407	−0.331 143	0.831 14

Table 2. Comparison of the binding energies $E_B = \frac{1}{2}\gamma - E$ (in au), obtained by using equation (4), with very accurate results from the literature (see text). The magnetic field strength γ is defined in units of 2.35×10^9 G. SO, Surmelian and O'Connell (1974); SV, Simola and Virtamo (1978); WR, Wunner and Ruder (1982); LZ, Le Guillou Zinn-Justin (1983); S, Silverman (1983).

	Present results						
γ	four variational parameters	five variational parameters	SO	SV	WR	LZ	S
0.2	0.590 38	0.590 38	0.5904		0.590 38	0.590 38	0.590 38
0.5	0.697 20	0.697 20	0.6972			0.697 21	0.697 21
0.8	0.782 25	0.782 27				0.782 28	
1	0.831 12	0.831 14	0.8312		0.831 17	0.831 16	0.831 16
2	1.022 06	1.022 13	1.0222	1.022	1.022 21	1.022 21	1.022 23
3	1.164 26	1.164 39			1.164 53	1.164 53	1.164 61
4	1.280 42	1.280 59			1.280 80		1.280 87
5	1.379 91	1.380 13	1.380			1.380 40	1.380 24
10	1.746 86	1.747 22	1.748		1.7478	1.7478	1.7436
15	2.006 77	2.007 21	2.005			2.0081	
20	2.213 80	2.214 31		2.2153	2.2154	2.2153	2.145
25	2.388 29	2.388 83	2.390	2.3889		2.3900	
40	2.798 57	2.799 19	2.795		2.8009		
50	3.015 08	3.015 74					
100	3.785 90	3.786 62	3.780	3.789	3.7891	3.790	5.2
200	4.721 82	4.722 51	4.690	4.727	4.7266	4.725	7.5
300	5.354 38	5.355 00	5.285		5.3603	5.355	
500	6.248 68	6.249 16					
1 000	7.649 50	7.649 75			7.6621	7.64	13
2 000	9.283 90	9.283 99		9.30	9.3045	9.27	7
3 000	10.355 74	10.355 77					
5 000	11.834 53	11.834 53					
10 000	14.081 67	14.081 67					
20 000	16.620 68	16.620 68		16.70		16.55	
50 000	20.450 78	20.450 78					

four (a, c, p and q; $s = 0$) and five (a, c, p, q and s) variational parameters. We briefly recall that the results of Surmelian and O'Connell (1974) were obtained from a variational calculation employing up to about 180 variational parameters. Simola and Virtamo (1978) used the adiabatic approximation together with an iterative, self-consistent, numerical determination of eigenvalues. Wunner and Ruder (1982) solved a system of Hartree-Fock-type equations. LeGuillou and Zinn-Justin (1983) used a 'suitable summation' requiring, as input, coefficients of standard perturbation theory up to the 62nd-order and 27-digit arithmetics. Silverman (1983) used a 'generalised Euler transformation'. Considering the relative sophistication of the aforementioned calculations, two points are noteworthy in our work: first, the energies are given in an analytical closed form; second, the numerical values obtained from (4) come very close to the best ones available. In particular note that our results (even with four variational parameters) are better than some of the results from the literature. Comparing our variational calculations with four and five parameters one sees that s is basically zero at both Coulomb and Landau limits, attaining its maximum value (for the cases shown in table 2) at $\gamma = 100$ when $a = 3.611$, $c = 49.06$, $p = 1.257$, $q = 5.893$ and $s = 0.2757$. In this case $\mathbb{K} = 26.947\,54$, $\mathbb{C} = -5.121\,14$ and $\mathbb{Z} = 24.386\,97$.

In conclusion, the factors $\exp[-\tfrac{1}{2}(a\xi + b\eta + c\xi\eta)]$ do indeed accelerate convergence in energy calculations of hydrogenic atoms in arbitrarily strong magnetic fields. The results reported here have stimulated us to calculate more strict bounds for the binding energy than reported in table 2. We hope to be able to report these soon.

Note added in proof. By 'scaling' the variational parameters according to $c = a^2\tilde{c}$, $p = a\tilde{c}\tilde{p}$, $q = (a\tilde{c})^2\tilde{q}$, $s = (a\tilde{c})^2\tilde{s}$ and noting that

$$Y_1^1(a, a, a^2\tilde{c}) = \frac{1}{a^3}\int_0^\infty \frac{t\,e^{-t}}{1+\tilde{c}t}\,dt$$

one may considerably simplify our equations (5)-(10). This makes the numerical work more efficient and stable. The expression for the energy may contain more than one stable minimum. Some of the energies in table 1 do not necessarily need to be the absolute minimum. However, the ordering in the table is always maintained.

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