

Zeeman diamagnetism in hydrogen: on variational *Ansätze* for arbitrary field strengths

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Received 18 April 1984, in final form 2 January 1985

Abstract. A field-dependent basis in parabolic coordinates is proposed as a very convenient set for arbitrary field strength variational calculations of diamagnetic properties of atoms and molecules. Basic characteristics of the basis are that it is exact in both Coulomb and Landau limits, and that matrix elements may be conveniently generated by using recurrence relations.

As is known, the calculation of the Zeeman effect in hydrogen with inclusion in the Hamiltonian of *both* linear and quadratic terms in the magnetic field strength is a quite difficult and hitherto unsolved problem. The basic difficulty arises from the non-separability of the Schrödinger equation and from the fact that as the field strength increases the symmetry of the problem changes from spherical to cylindrical. The recent upsurge of interest in this problem stems from the possibility of performing spectroscopic experiments with the so-called Rydberg states of atoms. Experimental and theoretical evidence collected in recent years suggests the possible existence of a dynamic symmetry for hydrogenic atoms in the presence of strong magnetic fields. These recent developments are discussed by, for example, Kleppner (1982), Kleppner *et al* (1983) and Gay and Delande (1983, 1984). The peculiarities of atoms in strong magnetic fields were also one of the subjects of a recent colloquium (Connerade *et al* 1982).

This paper now proposes a field-dependent basis for use in variational calculations of the magnetic properties of hydrogenic atoms. Up to now, a number of trial functions has already been used to investigate variationally the diamagnetism of hydrogen (see discussion below). Although some of these trial functions contained characteristics of both Coulomb and Landau limits, the great majority contained either a factor $\exp(-\alpha_C r)$ (Coulomb-type basis of spherical symmetry) or $\exp(-\alpha_L \rho^2)$ (Landau-type basis of cylindrical symmetry). (The parameters α_C and α_L are appropriate variational parameters.) As the symmetry is changed by the magnetic field, one must include more and more functions in the basis and the calculations eventually become impracticable. The large number of terms is basically needed to simulate the different symmetry (different exponential behaviour) as the magnetic field changes. By explicitly including both exponential factors in the trial functions (as done, for example, by Praddaude (1972) and Rau and Spruch (1976)) one would expect to be able to reduce the number of terms needed in the basis. This paper proposes a basis which has the particular characteristic of containing correctly the exact Coulomb and Landau solutions in the

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appropriate limits (i.e. at $B \rightarrow 0$ and $Z \rightarrow 0$, respectively) and is uniformly valid in the whole range $0 \leq B < \infty$. Furthermore, by using parabolic coordinates all matrix elements can be conveniently evaluated through recurrence relations.

The generic form of bound-state eigenfunctions may be written as

$$\psi(x, y, z) = \mathcal{N}f(x, y, z) \exp(-\frac{1}{2}g(x, y, z)) \quad (1)$$

where \mathcal{N} is an overall normalisation factor. The function $g(x, y, z)$, apart from constants with respect to x , y and z , is a 'polynomial' of fixed and low degree in x , y and z or involving simple functions of x , y and z , e.g. $r \equiv (x^2 + y^2 + z^2)^{1/2}$, $\rho^2 \equiv r^2 - z^2$, etc. The function $f(x, y, z)$ is a much more complicated 'polynomial' whose degree roughly increases with the excitation of the system. It is clear that the asymptotic behaviour of the eigenfunctions critically depends on the *functional* form of $g(x, y, z)$. As already mentioned, a number of previous investigators have studied the spectral properties of hydrogenic atoms in magnetic fields using either the Coulomb $g_C(x, y, z) = \alpha_C r$ (and $f(x, y, z)$ corresponding to Coulomb, Slater or Sturmian eigenfunctions) or the Landau $g_L(x, y, z) = \alpha_L \rho^2$ (with $f(x, y, z)$ corresponding to Landau eigenfunctions) bases. For specific results and references see the previously quoted work. A large number of recent references is also given by Rösner *et al* (1984). Although for limited ranges of field strength and atomic excitation these calculations produce excellent results, one eventually reaches a region where the inclusion of further terms in the expansion of the eigenfunctions is basically impracticable. What is needed therefore is to have a means of adiabatically interchanging $g_C(x, y, z) \rightleftharpoons g_L(x, y, z)$. The calculation of Rau *et al* (1975) and Rau and Spruch (1976) may be regarded as one attempt at performing this interchange. (Analytic approximations to quantities obtained with the eigenfunction of these authors have been recently presented by Wadehra (1983).) When proposing analytical expressions for $g(x, y, z)$, it is very important that they allow a large number of matrix elements to be easily evaluated. This point is important because the computation of many matrix elements is required in calculations involving eigenfunctions containing several polynomial terms. Of the many possible ways of performing the aforementioned adiabatic interchange we should like to propose the choice

$$g(x, y, z) = a(r+z) + b(r-z) + c(x^2 + y^2) \quad (2)$$

where a , b and c are non-negative variational parameters, as a form which allows all calculations to be performed analytically, and which constitutes a very good compromise between simplicity of the analytical work and accuracy of the results. We now proceed by using this ansatz to investigate explicitly spectral properties of a hydrogen atom placed in a uniform magnetic field.

The Hamiltonian corresponding to the present problem is given by (in atomic units such that $\hbar = m_e = e = 1$; the model and notation are consistent with those of Gallas (1984))

$$H = -\frac{1}{2}\nabla^2 - Z/r + \frac{1}{2}\gamma L_z + \frac{1}{8}\gamma^2(x^2 + y^2). \quad (3)$$

For the ground state one has $L_z = 0$. Actual calculations are particularly simple to perform in *parabolic* coordinates (ξ, η, φ) . In these coordinates the trial eigenfunction may be written as

$$\psi(\xi, \eta) = N\pi^{-1/2} \exp[-\frac{1}{2}(a\xi + b\eta + c\xi\eta)] \quad (4)$$

where the extra factor $\pi^{-1/2}$ was introduced to simplify the final expressions and the

trivial φ dependence was omitted. In parabolic coordinates, it is now a straightforward exercise to obtain

$$N^2 = 2/[Y_1^1(a, b, c) + Y_1^1(b, a, c)] \quad (5)$$

$$\langle 1/r \rangle = N^2 Y_1^0(a, b, c) = N^2 Y_1^0(b, a, c) \quad (6)$$

$$\langle \nabla^2 \rangle = -N^2 \{ (a+b) Y_1^0(a, b, c) + (c - \frac{1}{2}a^2) Y_1^1(a, b, c) + (c - \frac{1}{2}b^2) Y_1^1(b, a, c) \\ - (a+b)c Y_2^0(a, b, c) - \frac{1}{2}c^2 [Y_2^2(a, b, c) + Y_2^2(b, a, c)] \} \quad (7)$$

$$\langle x^2 + y^2 \rangle = \frac{1}{2} N^2 [Y_2^2(a, b, c) + Y_2^2(b, a, c)]. \quad (8)$$

It is also easy to see that an additional electric field $\mathbf{F}(\mathbf{F} \parallel \mathbf{B} \parallel \hat{z})$ would produce a Stark contribution given by

$$\langle z \rangle F = \frac{1}{4} F N^2 [Y_1^2(a, b, c) - Y_1^2(b, a, c)]. \quad (9)$$

All the above matrix elements have been expressed as functions of the quantities

$$Y_m^n(p, q, s) \equiv \int_0^\infty \frac{t^n \exp(-pt)}{(q+st)^m} dt. \quad (10)$$

An analytical expression for this integral may be found in, for example, equation (3.385-5), p 319, of the handbook by Gradshteyn and Ryzhik (1980). However, this expression is not always convenient to use in actual calculations. This is particularly true of excited states and/or more accurate variational functions, where one must consider a more complicated 'polynomial' $f(\xi, \eta)$ (in equation (1)) than the particular case $f(\xi, \eta) = 1$ discussed here. The amount of computer time required therefore depends very much on the ability to generate a large number of the quantities $Y_m^n(p, q, s)$ for some m and n and for many p, q and s . Using integration by parts and rearranging some of the formulae (3.383) of Gradshteyn and Ryzhik, it is trivial to show that

$$m! Y_{m+1}^n(p, q, s) = n! Y_{n+1}^m(q, p, s) \quad (11)$$

$$ms Y_{m+1}^n(p, q, s) = n Y_{m+1}^{n-1}(p, q, s) - p Y_m^n(p, q, s) \quad (12)$$

$$s Y_1^{n+1}(p, q, s) + q Y_1^n(p, q, s) = n! / p^{n+1} \quad (13)$$

$$msq^m Y_{m+1}^0(p, q, s) = 1 - pq^m Y_m^0(p, q, s) \quad m > 2. \quad (14)$$

These helpful relations allow one to reduce the evaluation of $Y_m^n(p, q, s)$ for all m and n to the calculation of just one $Y_{m^*}^{n^*}(p, q, s)$ for some arbitrary m^* and n^* . In the present case we found it convenient to express $Y_m^n(p, q, s)$ for all m and n as a function of $Y_1^1(p, q, s)$ which appears in the normalisation constant. This procedure obviously reduces the evaluation of all matrix elements to the evaluation of just $Y_1^1(p, q, s)$.

As may be easily verified, the Hamiltonian is totally symmetric with respect to the interchange $\xi \rightleftharpoons \eta$, while $\psi(\xi, \eta)$ in equation (4), in general, is not. Using the formulae just discussed, we calculated the field evolution of the ground state. As it turns out, for the ground state there is no spontaneous breaking of the ξ - η symmetry and our three-parameter variational calculation is, in fact, reduced to a two-parameter variational calculation. Within the numerical precision used we find $a = b$. Note, however, that we are investigating a variational space of dimension three and that rather than imposing $a = b$ we obtain this out of a general calculation. In particular, for $m \neq 0$ (m being the magnetic quantum number) we obtain $a \neq b$, a result that previous models

are not able to accommodate. Our results for $0.2 \leq \gamma \leq 5 \times 10^4$ (corresponding to $4.7 \times 10^8 \leq B \leq 11.75 \times 10^{13}$ G) are presented in table 1 together with some of the most accurate values taken from the literature. It should be noted that the values taken from the literature are the result of quite elaborate calculations. For example, those of Surmelian and O'Connell (1974, 1976) were obtained from a variational calculation employing up to about 180 variational parameters. (In table 1 we used the numbers given in table 2, p 34, of Surmelian (1974); a fit function to these data was published by Surmelian and O'Connell (1974, 1976).) Simola and Virtamo (1978) used the adiabatic approximation together with an iterative, self-consistent, numerical determination of eigenvalues. Wunner and Ruder (1982) (see also Rösner *et al* 1984, Forster *et al* 1984) adapted a computer code due to Froese Fischer (see Wunner and Ruder 1982) to solve a system of Hartree-Fock-type equations. They employed a Coulomb basis at low field strengths and Landau states at high fields. The numbers presented by LeGuillou and Zinn-Justin (1983) are obtained from a *suitable* summation method of perturbation theory in which one has to incorporate detailed information concerning the large-order asymptotic behaviour of the energy series. They use *as input* in their calculation coefficients of the perturbation theory up to the 62nd order and calculations have to be done with very high numerical precision (they used of the order of 27-digit arithmetics). Silverman (1983) used a 'generalised Euler transformation' as an alternative method of summing strongly divergent perturbation series. His results are very good up to about $\gamma \sim 10$. However, as he points out, there is as yet insufficient evidence to draw any conclusions about possible bounds furnished by his interesting method. All the results of the first four impressive works mentioned are in perfect agreement with each other up to about $\gamma = 100$. For $\gamma > 100$ the results of Surmelian and O'Connell seem to be too low compared with those of Simola and Virtamo, Wunner and Ruder and LeGuillou and Zinn-Justin, although they still agree to two significant figures. For $\gamma > 1000$ there is agreement 'only' up to two significant figures. It is interesting to note that what is being compared is the binding energies $E_B = \frac{1}{2}\gamma - E$. In this way one magnifies differences that otherwise remain hidden after several correct digits in the eigenvalues. We find it remarkable that our modest two-parameter trial function (equation (4) with $a = b$) remains fairly accurate over the whole field interval considered.

From table 1 it is seen that $c = \gamma/2$ (the exact value for the pure Landau problem) is usually a very good *starting value* for determining c . Note also the behaviour of the parameters a and b . They actually increase from the field-free Coulomb values $a = b = 1$, explicitly showing that although the role of the Coulomb term diminishes, it never vanishes. It is also important to realise that all results presented in table 1 are based on a non-relativistic model. A limit on the magnetic field strength for the model to remain reliable may easily be obtained by estimating the magnetic field required to produce an energy difference of mc^2 between neighbouring Landau levels. This defines the threshold $B_{th} = m^2 c^3 / e\hbar \approx 4.4 \times 10^{13}$ G ($\gamma_{th} \approx 18700$). Furthermore, note that the results in table 1 were derived on the assumption that the proton is infinitely heavy. For the ground state this assumption is always a good one. (The explicit effect of this approximation is discussed in detail by Wunner and Ruder (1982).)

In table 2 we present a comparison of our results with those obtained from calculations requiring about the same computational effort as ours. The results of Rau *et al* (1975) correspond in fact to a constrained calculation with our equation (4). (They fix $c = \gamma/2$ and consider a one-parameter $a \equiv b$ variation.) Bhaduri *et al* (1977) used a one-parameter trial function obtained by solving a Schrödinger-type differential

Table 1. Comparison of the binding energies $E_n = \gamma/2 - E$, obtained by using equation (4), with very accurate results from the literature (see text). All numbers are given in a.u. The magnetic field strength γ is defined in units of 2.35×10^9 G. SO, Surmelian and O'Connell (1974, 1976); SV, Simola and Vitamo (1978); WR, Wunner and Ruder (1982); LZ, LeGuillou and Zinn-Justin (1983); S, Silverman (1983).

γ	$a = b$	c	E	Present results	SO	SV	WR	LZ	S
0.2	1.0028	0.0158	-0.490 36	0.590 36	0.5904		0.590 38	0.590 38	0.590 38
0.5	1.0081	0.0853	-0.446 82	0.696 8	0.6972		0.697 21	0.697 21	0.697 21
0.8	1.0219	0.1704	-0.381 21	0.781 2			0.782 28	0.782 28	
1.0	1.0324	0.2319	-0.329 56	0.829 6	0.8312		0.831 17	0.831 16	0.831 16
2.0	1.0840	0.5664	-0.017 63	1.018	1.0222	1.022	1.022 21	1.022 21	1.022 23
3.0	1.1283	0.9259	0.342 97	1.157			1.164 53	1.164 53	1.164 61
4.0	1.1659	1.300	0.729 45	1.271			1.280 80	1.280 80	1.280 87
5.0	1.1985	1.684	1.132 4	1.368	1.380		1.380 40	1.380 40	1.380 24
10.0	1.3177	3.693	3.275 9	1.724	1.748		1.747 8	1.747 8	1.743 6
15.0	1.3994	5.788	5.524 2	1.976	2.005		2.008 1	2.008 1	
20.0	1.4624	7.933	7.824 3	2.176			2.215 4	2.215 3	2.145
25.0	1.5142	10.11	10.156	2.344	2.390	2.3889	2.800 9	2.390 0	
40.0	1.6310	16.78	17.262	2.738	2.795				
50.0	1.6902	21.30	22.054	2.946					
100.0	1.8891	44.36	46.317	3.683	3.780	3.789	3.789 1	3.790	5.2
200.0	2.1107	91.56	95.424	4.576	4.690	4.727	4.726 6	4.725	7.5
300.0	2.2510	139.4	144.82	5.178	5.285		5.360 3	5.355	
500.0	2.4392	236.0	243.97	6.029					
1 000.0	2.7154	479.8	492.64	7.364			7.662 1	7.64	13
2 000.0	3.0161	971.4	991.07	8.925		9.30	9.304 5	9.27	7
3 000.0	3.2038	1 465.1	1 490.0	9.953					
5 000.0	3.4526	2 455.6	2 488.6	11.38					
10 000.0	3.8125	4 939.3	4 986.5	13.55					
20 000.0	4.1978	9 918.0	9 984.0	16.02		16.70		16.55	
50 000.0	4.7449	24 880.5	24 980.2	19.77					

Table 2. Comparison of our binding energies (au) with those obtained from calculations requiring about the same computational effort as ours. The 'exact' values are from Wunner and Ruder (1982) (see our table 1). The present results as well as those of Wadehra (1978) are from variational calculations employing two variational parameters. The results in the last three columns are from one-parameter variational calculations. W, Wadehra (1978); B, Bhaduri *et al* (1977); RS, Rau and Spruch (1976); M, Mueller *et al* (1971).

γ	'Exact'	This work	W	B	RS†	M
2	1.022	1.018		1.01	0.99	0.89
20	2.215	2.176	2.09	2.16	2.05	2.09
100	3.789	3.683	3.58	3.63	3.47	3.59
300	5.360	5.178	5.10	5.07	4.90	5.04
1000	7.662	7.364	7.37	7.12	7.06	7.06

† These numbers are also given by Rau *et al* (1975).

equation generated with the variational principle. Note that their calculation is more than just a one-parameter variational calculation. Wadehra (1978) uses a two-parameter trial function which is a combination of 1s and 2s orbitals with a ground-state Landau function.

The electronic charge density in the plane $\xi\eta$ is defined by

$$\text{density} \equiv \frac{1}{4}(\xi + \eta)\psi^2(\xi, \eta). \quad (15)$$

Figure 1 shows this density, conveniently renormalised, for several values of the magnetic field strength γ . This figure clearly shows that the effect of the field is to compress the eigenfunctions symmetrically along the $z = 0$ plane (i.e. along the direction $\xi = \eta$). Note also that the charge is concentrated by the field in two symmetric regions. In connection with the so-called quasi-Landau spectrum (see, for example, Gallas *et al* 1983 and references therein), it should be particularly interesting to have similar plots, but for excited states. For high field strengths the eigenfunction is basically confined along the directions $\xi = 0$ and $\eta = 0$.

In summary, this paper proposes using parabolic coordinates and factors $\exp[-\frac{1}{2}(a\xi + b\eta + c\xi\eta)]$ in eigenfunctions describing atoms placed in uniform magnetic fields as a means of simplifying analytical work and abbreviating convergence properties of variational calculations. The prototype eigenfunction of an arbitrary state is of the generic form

$$\psi = \exp(\pm im\varphi)[\exp[-\frac{1}{2}(a\xi + b\eta + c\xi\eta)]] \left(\sum_{i=0}^{\infty} \alpha_i \xi^i + \sum_{j=0}^{\infty} \beta_j \eta^j + \sum_{k=0}^{\infty} \delta_k (\xi\eta)^k \right) \quad (16)$$

with α_i , β_j and δ_k being variational parameters. (From the present results one is tempted to believe that for the ground state the identity $\alpha_i = \beta_i$ holds.) The substitution of the power series in the large parentheses by the more general expansion $\sum_{i,j=0}^{\infty} d_{ij} \xi^i \eta^j$ presents no intrinsic difficulty and will render a more flexible trial function. All matrix elements arising from using equation (16) can be conveniently evaluated using our formulae (11)–(14). It would be interesting to know how many parameters α , β and δ are necessary to obtain results with, say, the same accuracy of the very precise ones displayed in table 1. Furthermore, being accurate in the whole field interval $0 \leq B < \infty$, the present eigenfunctions should also be very helpful for investigating molecular properties. These studies are in progress.

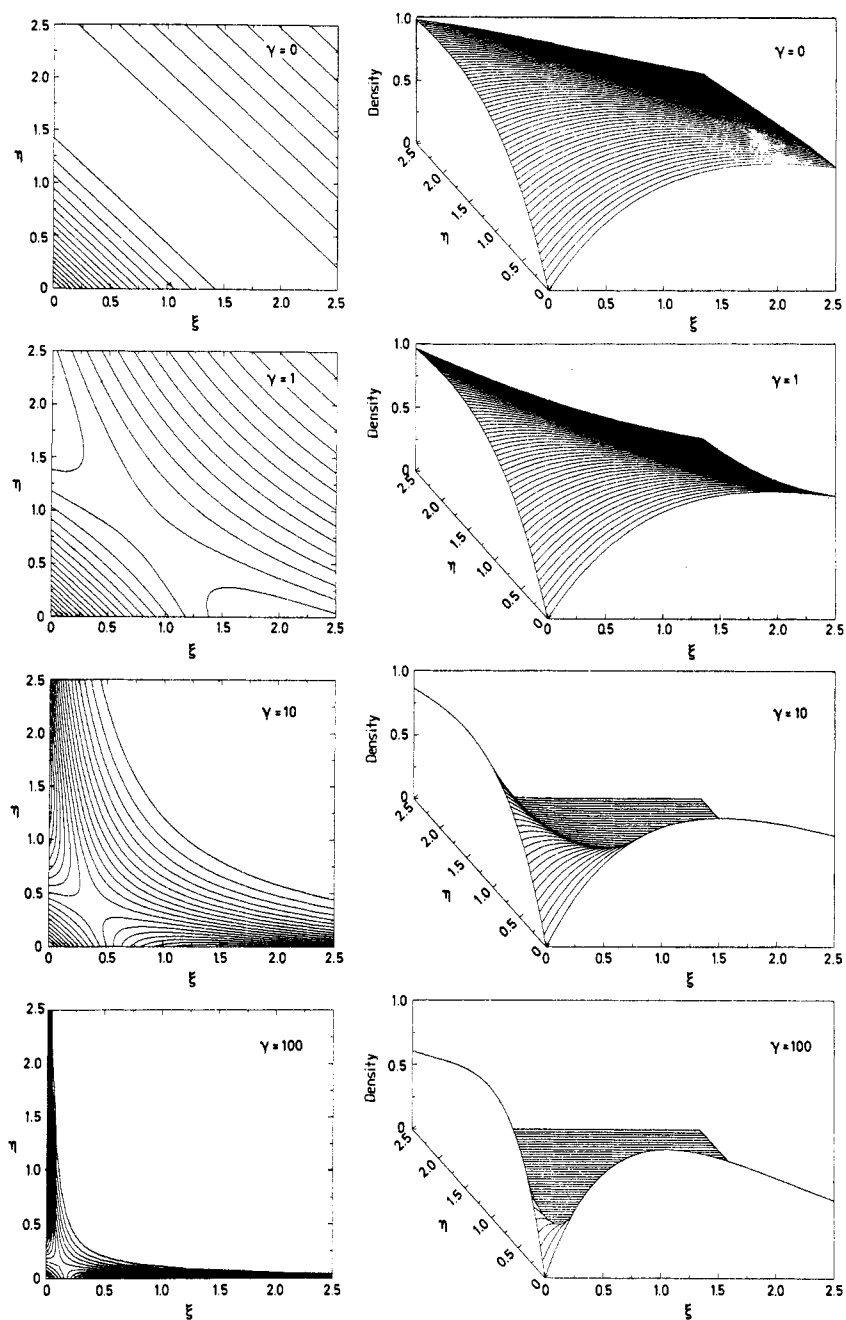


Figure 1. Plots of the electronic charge density (equation (15)) as a function of the magnetic field strength γ ($\gamma=1$ corresponds to $B=2.35 \times 10^9$ G). The coordinates $\xi=r+z$ and $\eta=r-z$ are measured in au. The plots on the left-hand side are obtained by intersecting the corresponding 3D views on the right-hand side with a family of equidistant planes parallel to the $\xi\eta$ plane. Besides the strong confinement caused by the field, note the *symmetrical* redistribution of the charge (see the text).

Note added in proof. After this work was submitted for publication, a paper by Cohen and Kais (1984) appeared. This treats the Zeeman problem using variational methods quite similar to ours.

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