# Simple basis for hydrogenic atoms in magnetic fields

Jason A. C. Gallas

*Max-Planck-Institut für Quantenoptik, Forschungsgelände, D-8046 Garching bei München,*
*Federal Republic of Germany*
*and Departamento de Física, Universidade Federal de Santa Catarina, 88000 Florianópolis,*
*Santa Catarina, Brasil*

(Received 8 July 1983)

A field-dependent hydrogenic basis is used to obtain the evolution of the energy spectrum of atoms in strong ($\sim 10^8$ G) and uniform magnetic fields. The basis allows results to be derived analytically. Numerical values for the first 13 excited states of hydrogen are found to be in very good agreement with much more elaborate calculations of Smith *et al.* and of Brandi. In addition, the possibility of having a remnant type of degeneracy in the presence of the magnetic field is investigated.

## I. INTRODUCTION

In recent years the challenge of the nonseparable diamagnetic Zeeman interaction has attracted much attention. Besides the well-known applications in astrophysics and condensed matter, the recent upsurge of interest in this basic and still unsolved problem of theoretical physics is motivated by several empirical discoveries and growing accumulation of evidence that a dynamic symmetry exists when hydrogenic atoms are placed in a uniform magnetic field. References 1–5 give some recent representative works on this subject where the motivation and difficulties of this problem are further discussed.

The purpose of the present paper is to present a simple and reliable way to follow, from the Coulomb limit, the field evolution of the energy spectrum of hydrogenic atoms placed in a uniform and strong magnetic field. The basic idea behind the present approach is the physically reasonable assumption that the main effect of the magnetic field on the atomic eigenfunctions, as it adiabatically increases from zero, is to compress them. In other words, we assume that the $nlm$ field-free eigenfunctions continue to basically represent the $nlm$ state[6] in the presence of the field. The primary effect of the field on the quantum states would be to introduce distortions to them and we simulate such distortions by introducing one single field-dependent nonlinear variational parameter in the radial part of the eigenfunction. As will be seen below, application of this idea produces remarkably good results, considering its simplicity. Furthermore, all results are obtained analytically. For the three lowest $n$ manifolds (for which results of elaborate calculations are available in the literature) the present *analytical approach* is reliable for the study of atoms in fields typical[7] of white dwarfs (up to $\sim 2.3 \times 10^8$ G). In particular, they compare fairly well with the much more elaborate calculations of Smith *et al.*[8] and of Brandi.[9] With "effective atomic units" used in the usual way, these results can easily be applied to laboratory field strengths, e.g., in hydrogenic excitons.

## II. THEORY

With spin and relativistic effects neglected, the Hamiltonian for a hydrogen atom in a uniform magnetic field characterized by a vector potential $\vec{A}$ is

$$H = \frac{1}{2m_e}\left[\vec{p} + \frac{e}{c}\vec{A}\right]^2 - \frac{e^2}{r} . \tag{1}$$

Assuming the magnetic field $\vec{B}$ to be along the $z$ direction [$\vec{B} = (0,0,B)$], choosing the usual gauge $\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}$, spherical coordinates $(r,\theta,\phi)$, and atomic units such that $\hbar = e = m_e = 1$, one gets

$$H = H_0 + H_{\text{mag}} = H_0 + \frac{1}{2}\gamma L_z + \frac{1}{8}\gamma^2 r^2 \sin^2\theta , \tag{2}$$

where $H_0 = \frac{1}{2}p^2 - 1/r$ is the field-free Hamiltonian, $L_z$ is the $z$ component of the angular momentum, and $\gamma = eB/(m_e c)$. In the units used, the parameter $\gamma$ is equal to the cyclotron frequency. It measures the magnetic field strength in units of $2.35 \times 10^9$ G or, equivalently, $2.35 \times 10^5$ T.

As mentioned before, the basic idea behind the present calculation of the Zeeman diamagnetism is to simulate the field compression of the atomic eigenfunctions through a nonlinear variational parameter which will be called $\beta$. This parameter plays essentially the same role as the "effective-charge" parameter common in molecular calculations. We therefore define the basis $|nlm\rangle = R_{nl}(r)Y_l^m(\theta,\phi)$, where $R_{nl}(r)Y_l^m(\theta,\phi)$ are the usual normalized eigensolutions of the field-free Hamiltonian $H_0$ [defined in Eq. (2)] in which the nuclear charge was replaced by $\beta$. For $\beta \neq 1$ this basis is not completely orthogonal. Using these eigensolutions, one can derive the energy in the standard way

$$E_{nlm}(\beta) = \langle nlm | H | nlm \rangle = E_0 + E_{\text{mag}} . \tag{3}$$

The paramagnetic contribution is given by

$$\langle nlm | \tfrac{1}{2}\gamma L_z | nlm \rangle = \tfrac{1}{2}\gamma m . \tag{4}$$

The diamagnetic contribution is also easy to evaluate

$$\tfrac{1}{8}\gamma^2 \langle nlm \mid r^2 \sin^2\theta \mid nlm \rangle = \tfrac{1}{8}\gamma^2 \langle nl \mid r^2 \mid nl \rangle \langle lm \mid \sin^2\theta \mid lm \rangle \ , \tag{5}$$

$$\langle lm \mid \sin^2\theta \mid lm \rangle = 1 - \langle lm \mid \cos^2\theta \mid lm \rangle = 1 - \left[ \frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)} + \frac{(l+m)(l-m)}{(2l+1)(2l-1)} \right] = 2\frac{l(l+1)+m^2-1}{(2l+3)(2l-1)} \ , \tag{6}$$

$$\langle nl \mid r^2 \mid nl \rangle = \frac{1}{2}\frac{n^2}{\beta^2}[5n^2 - 3l(l+1)+1] \ . \tag{7}$$

In evaluating $E_0$ one should pay due attention to the fact that $\mid nlm \rangle$ is not an eigenfunction of $\tfrac{1}{2}p^2 - 1/r$ but, instead, of $\tfrac{1}{2}p^2 - \beta/r$. Hence,

$$E_0 = \left\langle nlm \left| \tfrac{1}{2}p^2 - \frac{1}{r} \right| nlm \right\rangle$$

$$= \left\langle nlm \left| \tfrac{1}{2}p^2 - \frac{\beta}{r} \right| nlm \right\rangle + (\beta - 1)\left\langle nlm \left| \frac{1}{r} \right| nlm \right\rangle$$

$$= -\frac{\beta^2}{2n^2} + (\beta - 1)\frac{\beta}{n^2} = \frac{1}{2n^2}(\beta^2 - 2\beta) \ . \tag{8}$$

For $\beta = 1$, $E_0$ reduces to the well-known hydrogenic energy spectrum, as it should. Collecting all terms together, it follows that

$$E_{nlm}(\beta) = a\beta^2 - 2a\beta + b + c/\beta^2 \ , \tag{9a}$$

where

$$a = \tfrac{1}{2}n^{-2} \ , \tag{9b}$$

$$b = \tfrac{1}{2}\gamma m \ , \tag{9c}$$

$$c = \tfrac{1}{8}\gamma^2 f(n,l,m) \ , \tag{9d}$$

$$f(n,l,m) = n^2[5n^2 - 3l(l+1)+1][l(l+1)+m^2-1]$$
$$\times [4l(l+1)-3]^{-1} \ . \tag{9e}$$

This equation is the basic equation of the present paper. The field evolution of an $nlm$ state[6] can be obtained by solving the equation $\partial E_{nlm}/\partial\beta = 0$ for the optimum parameter $\beta$. This amounts to solving the quartic

$$\beta^3(\beta - 1) - \frac{c}{a} = 0 \tag{10}$$

for the unique positive root $\beta_{\text{opt}}$. Before proceeding, a few comments are in order. For $\beta = 1$ Eq. (9) reduces to the

result obtained by Guth[10(a)] and by Schiff and Snyder[10(b)] using first-order perturbation theory. As discussed by Ruder et al.,[11] the perturbative result is strictly only valid for nondegenerate states. In contrast, the present variational result has no such restriction. By comparing results from the perturbative equation with the ones from a much more elaborate variational calculation, Smith et al.[8] concluded that for the $n=2$ and 3 manifolds, perturbative results are inadequate for $B$ values of about $10^8$ and $3 \times 10^7$ G, respectively. As will be shown in the next section, Eq. (9) allows the validity of the results for the aforementioned manifolds to be easily extended by 1 order of magnitude at least. It is also interesting to note that, with the paramagnetic-term $b$ omitted, Eq. (9) obeys the same scaling relation recently obtained for Rydberg atoms in magnetic fields.[12]

### III. DISCUSSION

There have been a number of calculations on the effect of a magnetic field on the spectrum of hydrogen. These calculations, in a general manner, can be divided into two classes: (a) high-field calculations, when one starts with Landau-type eigenfunctions and tries to follow the field evolution of the levels as the field is adiabatically decreased, or (b) low-field calculations, where Coulomb-type eigenfunctions are employed and one follows the adiabatic changes as the field is increased. It is clear that our present approach fits into this second generic type. In general, it is quite hard to estimate the error present in a calculation of any type. We therefore try to assess the limit of validity of the present calculation by systematic comparison with results from the literature. We will be mainly concerned with members of the $n=2$ and 3 manifolds, for which, at least, some results have already been

TABLE I. Some energies (in a.u.) for $B = 2.35 \times 10^8$ G ($\gamma = 0.1$).

| State | First-order perturbation theory ($\beta = 1$) | This work (minimizing $\beta$) | Killingbeck (Ref. 14) | Praddaude (Ref. 13) |
|---|---|---|---|---|
| $1s$ | $-0.497\,500$ | $-0.497\,512$ | $-0.497\,521\,7$ | $-0.497\,525$ |
| $2s$ | $-0.090\,000$ | $-0.095\,822$ | $-0.095\,653\,0$ | $-0.098\,085$ |
| $2p_0$ | $-0.100\,000$ | $-0.111\,363$ | $-0.111\,752\,6$ | $-0.112\,410$ |
| $2p_{-1}$ | $-0.145\,000$ | $-0.149\,509$ | $-0.150\,522\,0$ | $-0.150\,845$ |
| $3d_{-1}$ | $-0.015\,556$ | $-0.051\,678$ | $-0.054\,308\,9$ | $-0.057\,810$ |
| $3d_{-2}$ | $-0.020\,556$ | $-0.082\,822$ | $-0.086\,574\,9$ | $-0.087\,835$ |

TABLE II. Energies (in a.u.) for more intense field strengths ($\gamma = 0.0425$, 0.2127, and 0.425).

| State | $B$ (G) | Peek and Katriel (Ref. 15) | This work (minimizing $\beta$) | Cohen and Herman (Ref. 16) |
|---|---|---|---|---|
| 1s | $1\times10^8$ | $-0.499\,548$ | $-0.499\,548$ | |
| | $5\times10^8$ | $-0.489\,06$ | $-0.488\,92$ | |
| | $1\times10^9$ | $-0.459\,68$ | $-0.458\,02$ | |
| 2s | $1\times10^8$ | $-0.1207$ | $-0.118\,943$ | $-0.119\,08$ |
| | $5\times10^8$ | $-0.055\,08$ | $-0.024\,41$ | $-0.033\,49$ |
| | $1\times10^9$ | $0.060\,80$ | $0.150\,35$ | $0.122\,16$ |
| $2p_0$ | $1\times10^8$ | $-0.122\,37$ | $-0.122\,339$ | $-0.122\,40$ |
| | $5\times10^8$ | $-0.077\,58$ | $-0.073\,78$ | $-0.079\,96$ |
| | $1\times10^9$ | $0.010\,18$ | $0.025\,80$ | $0.003\,61$ |
| $2p_1$ | $1\times10^8$ | $-0.098\,59$ | $-0.098\,50$ | $-0.098\,60$ |
| | $5\times10^8$ | $0.064\,73$ | $0.070\,67$ | $0.063\,92$ |
| | $1\times10^9$ | $0.3152$ | $0.3352$ | $0.313\,36$ |

published. For these 13 states the high-field regime starts at about $3\times10^7$ G (i.e., at $\gamma \cong 0.01$).

Table I shows some energy values for $\gamma = 0.1$. The first column shows the result of first-order perturbation theory [Eq. (9) with $\beta = 1$]. The second column contains the result as obtained from Eq. (9) after minimization with

respect to $\beta$. These values are compared with the corresponding ones of Praddaude[13] (variational calculation using Laguerre polynomials in cylindrical coordinates) and of Killingbeck[14] (partitioning of the Zeeman Hamiltonian plus series method). One clearly sees the effect of the $\beta$ minimization over the perturbative calculations, especially

TABLE III. Comparison of the energy spectrum [in Rydberg units ($=1/2$ a.u.)] in a uniform magnetic field for the 13 lowest states above the ground state. Upper line, present results; lower line, Smith et al. (Ref. 8). For the 3s state the present results are smaller up to $\gamma = 0.05$.

| State | $B=1.175\times10^7$ G $\gamma=0.005$ | $4.700\times10^7$ G 0.02 | $1.175\times10^8$ G 0.05 | $2.350\times10^8$ G 0.1 | $4.700\times10^8$ G 0.2 |
|---|---|---|---|---|---|
| 2s | $-0.2498$ | $-0.2472$ | $-0.2335$ | $-0.1916$ | $-0.067\,15$ |
| | $-0.2498$ | $-0.2472$ | $-0.2340$ | | $-0.097\,85$ |
| $2p_{-1}$ | $-0.2548$ | $-0.2676$ | $-0.2857$ | $-0.2990$ | $-0.2879$ |
| | $-0.2549$ | $-0.2676$ | $-0.2861$ | | $-0.3007$ |
| $2p_0$ | $-0.2499$ | $-0.2488$ | $-0.2427$ | $-0.2227$ | $-0.1575$ |
| | $-0.2499$ | $-0.2488$ | $-0.2429$ | | $-0.1702$ |
| $2p_1$ | $-0.2448$ | $-0.2276$ | $-0.1857$ | $-0.0990$ | $0.1120$ |
| | $-0.2448$ | $-0.2276$ | $-0.1861$ | | |
| 3s | $-0.1102$ | $-0.098\,60$ | $-0.050\,25$ | $0.062\,47$ | $0.3339$ |
| | $-0.1101$ | $-0.097\,27$ | $-0.049\,39$ | | $0.1778$ |
| $3p_{-1}$ | $-0.1152$ | $-0.1181$ | $-0.098\,14$ | $-0.032\,18$ | $0.1464$ |
| | $-0.1152$ | $-0.1182$ | $-0.1025$ | | $0.021\,74$ |
| $3p_0$ | $-0.1106$ | $-0.1043$ | $-0.0755$ | $-0.0033$ | $0.1782$ |
| | $-0.1106$ | $-0.1047$ | $-0.082\,76$ | | $0.0521$ |
| $3p_1$ | $-0.1052$ | $-0.078\,10$ | $0.001\,86$ | $0.1678$ | $0.5464$ |
| | $-0.1052$ | $-0.084\,16$ | | | |
| $3d_{-2}$ | $-0.1204$ | $-0.1411$ | $-0.1612$ | $-0.1656$ | $-0.1318$ |
| | $-0.1204$ | $-0.1414$ | $-0.1635$ | | $-0.1606$ |
| $3d_{-1}$ | $-0.1156$ | $-0.1243$ | $-0.1255$ | $-0.1033$ | $-0.021\,76$ |
| | $-0.1156$ | $-0.1245$ | $-0.1282$ | | $-0.062\,25$ |
| $3d_0$ | $-0.1107$ | $-0.1053$ | $-0.080\,63$ | $-0.017\,27$ | $0.1444$ |
| | $-0.1108$ | $-0.1072$ | $-0.090\,96$ | | $0.058\,43$ |
| $3d_1$ | $-0.1056$ | $-0.084\,31$ | $-0.025\,50$ | $0.096\,64$ | $0.3782$ |
| | $-0.1056$ | $-0.084\,49$ | | | |
| $3d_2$ | $-0.1004$ | $-0.061\,14$ | $0.038\,79$ | $0.2343$ | $0.6681$ |
| | $-0.1004$ | $-0.078\,21$ | | | |

for the $3d$ states. Our results are in good agreement with the other two calculations.

Table II shows a similar comparison, at higher-field strengths, for some states as calculated by Peek and Katriel[15] and by Cohen and Herman.[16] The first authors numerically solved a pair of self-consistent equations (exact at zero field) in prolate spheroidal coordinates, while Cohen and Herman used a combination of perturbation theory with a variational calculation. Again, fair agreement is obtained by our one-parameter variational results. As a final comparison, Table III shows the field evolution of the 13 lowest states above the ground state. In this table our results are compared with the ones obtained by Smith et al.[8] with an elaborate variational calculation using an eigenfunction made of up to 12 Slater-type orbitals. These same 13 states in the same field range were also investigated by Brandi.[9] He used an hydrogenic basis with $ns$, $n'd$, and $n''p$ functions with $1 \leq n \leq 6$, $2 \leq n'' \leq 7$, and $3 \leq n' \leq 8$. The results obtained by these authors are in very good agreement with each other, as can be seen from Fig. 1 of Brandi. Both results were given for fields of up to $2.35 \times 10^8$ G ($\gamma = 0.1$), which are typical of white dwarfs. Once again one sees that the results obtained from the trivial one-parameter minimization of Eq. (9) are in good agreement with the much more elaborate calculations. It is worth pointing out that in this range perturbative calculations [Eq. (9) with $\beta = 1$] can be off by a factor of up to 18. In Table III we have also included positive energies although, owing to the very different boundary conditions of the problem in this region, they are expected to lose accuracy quickly. In general, the results of Eq. (9) with $\beta$ minimization tend to remain fairly accurate as long as the energies are below the autoionization limit ($E = 0$). This agreement is particularly interesting if one remembers that the basis being used is not completely orthogonal. We believe the above comparison to demonstrate the usefulness of the "$\beta$-scaled" $|nlm\rangle$ hydrogenic basis in deriving reliable *analytical* results. *Numerical* work with this basis has already been done by Brandi and Koiller.[17] They used a variational eigenfunction made of up to 35 $|nlm\rangle$ states to investigate the diamagnetism of hydrogen. As a consequence (and in contrast to the present case), they had to diagonalize large matrices with a computer. Perhaps one should at this point recall that the computational difficulty to calculate the field evolution of the quantum states in the presence of the field amounts to solving Eq. (10) for the positive root, indeed a trivial task. We also remark that the fact that our one-

parameter variational functions coincide in form with the field-free hydrogenic eigenfunctions makes it relatively easy to obtain matrix elements and, therefore, bound-bound as well as bound-free (photoionization) transition probabilities. These and some other results will be presented elsewhere.

To conclude, we should like to call attention to the very interesting possibility of having "remnant" degeneracies in the $E_{nlm}(\beta)$ of Eq. (9). Within an $n$ manifold, this corresponds to having cases such that $f(n,l,m) = f(n,l',m')$, $f(n,l,m)$ being defined in Eq. (9e). The paramagnetic contribution [Eq. (9c)] tells us that we must have $m = m'$ and, therefore, should look for $f(n,l,m) = f(n,l',m)$. From this, one obtains a very simple equation to determine $l'$, namely,

$$x^2 - 2Px - Q = 0 , \tag{11a}$$

where $x = l'(l'+1)$ and

$$P = \tfrac{1}{6}(\nu - 3\mu - 4N/D) , \quad Q = \tfrac{1}{3}\nu\mu + N/D , \tag{11b}$$

$$N = [\nu - 3l(l+1)][l(l+1)+\mu] , \quad D = 4l(l+1) - 3 , \tag{11c}$$

$$\nu = 5n^2 + 1 , \quad \mu = m^2 - 1 . \tag{11d}$$

To be a solution of the physical problem, besides being a positive root of Eq. (11a), $x$ must be an integer and a member of the very particular set $x = 0, 2, 6, 12, 20, \ldots, n(n-1)$. It is easy to see that, e.g., $f(4,1,0) = f(4,2,0)$, and therefore that these states, in our approximate solution, ought to *remain degenerate at any field strength*. By choosing $\beta = 1$ in Eq. (9), this conclusion can also be regarded as a consequence of first-order perturbation theory. A natural question arises whether this type of degeneracy would persist in a more elaborate calculation (e.g., in a higher-order perturbative treatment) or not. At any rate, in a limited but still wide field range, a more elaborate calculation is not expected to affect the above conclusions very much.

## ACKNOWLEDGMENTS

[1]D. Kleppner, *Laser-Plasma Interaction,* Les Houches XXXIV, edited by R. Balian (North-Holland, Amsterdam, 1982); M. L. Zimmerman, J. C. Castro, and D. Kleppner, Phys. Rev. Lett. **40**, 1083 (1978); J. C. Castro, M. L. Zimmerman, R. G. Hulet, D. Kleppner, and R. R. Freeman, *ibid.* **45**, 1780 (1980); M. L. Zimmerman, R. G. Hulet, and D. Kleppner, Phys. Rev. A **27**, 2731 (1983).

[2]J.-C. Gay, in *Progress in Atomic Spectroscopy, Part C* (Plenum, New York, in press); D. Delande, C. Chardonet, F. Biraben, and J.-C. Gay, J. Phys. (Paris), Colloq. **43**, C2-97 (1982).

[3]E. A. Solov'ev, Zh. Eksp. Teor. Fiz. Pis'ma Red. **34**, 278 (1981) [JETP Lett. **34**, 265 (1981)]; E. A. Solov'ev, Zh. Eksp. Teor.

Fiz. **82**, 1762 (1982) [Sov. Phys.—JETP **55**, 1017 (1982)].

[4]P. A. Braun, Zh. Eksp. Teor. Fiz. **84**, 850 (1983) [Sov. Phys.—JETP (English translation not yet available)]; A. P. Kazantsev and V. L. Pokrovsky, Zh. Eksp. Teor. Fiz. Pis'ma Red. **37**, 471 (1983) [JETP Lett. (English translation not yet available)]; A. P. Kazantsev, V. L. Pokrovsky, and J. Bergou, Central Research Institute for Physics, Budapest, Report No. KFKI-1983-01 (unpublished); A. P. Kazantsev and V. L. Pokrovsky, J. Phys. B **16**, L601 (1983).

[5]D. R. Herrick, Phys. Rev. A **26**, 323 (1982); M. Yu. Sumetskii, Zh. Eksp. Teor. Fiz. Pis'ma Red. **36**, 24 (1982) [JETP Lett. **36**, 27 (1982)]; J. B. Delos, S. K. Knudson, and D. W. Noid,

Phys. Rev. Lett. 50, 579 (1983); *ibid.* 51, 325(E) (1983); Phys. Rev. A 28, 7 (1983); D. Richards, J. Phys. B 16, 749 (1983); M. Robnik, J. Phys. (Paris), Colloq. 43, C2-45 (1982); A. Harada and H. Hasegawa, J. Phys. A 16, L503 (1983).

[6]Strictly, the quantum numbers *nlm* are only defined in the absence of the field. In the presence of the field we use them as a loose but useful label.

[7]R. H. Garstang, J. Phys. (Paris), Colloq. 43, C2-19 (1982).

[8]E. R. Smith, R. J. W. Henry, G. L. Surmelian, R. F. O'Connell, and A. K. Rajagopal, Phys. Rev. D 6, 3700 (1972); the numbers in our Table III are from G. L. Surmelian, Ph.D. thesis, Louisiana State University, 1974 (unpublished), p. 35, Table 3.

[9]H. S. Brandi, Phys. Rev. A 11, 1835 (1975); see also R. R. dos Santos and H. S. Brandi, *ibid.* 13, 1970 (1976).

[10](a) E. Guth, Z. Phys. 58, 368 (1929); (b) L. I. Schiff and H. Snyder, Phys. Rev. 55, 59 (1939); (c) further references are given by R. H. Garstang, Rep. Prog. Phys. 40, 105 (1977).

[11]H. Ruder, G. Wunner, H. Herold, and M. Reinecke, J. Phys. B 14, L45 (1981).

[12]J. A. C. Gallas, E. Gerck, and R. F. O'Connell, Phys. Rev. Lett. 50, 324 (1983).

[13]H. C. Praddaude, Phys. Rev. A 6, 1321 (1972).

[14]J. Killingbeck, J. Phys. B 14, L461 (1981).

[15]J. M. Peek and J. Katriel, Phys. Rev. A 21, 413 (1980).

[16]M. Cohen and G. Herman, J. Phys. B 14, 2761 (1981).

[17]H. S. Brandi and B. Koiller, Can. J. Phys. 56, 1545 (1978).