Addendum to "Hydrogen atoms in strong magnetic fields"*

R. R. dos Santos and H. S. Brandi
Pontificia Universidade Católica do Rio de Janeiro, Departamento de Fisica, Rua Marquês de São Vicente 225, Gávea, Rio de Janeiro, Brasil

(Received 22 September 1975)

On the basis of a variational scheme for a trial wave function given as an expansion of the exact solutions of the three-dimensional isotropic harmonic oscillator, we have calculated the energies for the 14 lowest energy states of a hydrogen atom in the presence of magnetic fields ranging from approximately 10^9 to 10^{11} G. We also discuss the connection between the low- and high-field energy spectra based upon the noncrossing rule.

In a recent article one of us (HSB) proposed a variational scheme to obtain the solutions of the Schrödinger equation for hydrogen atoms in strong magnetic fields. The solution assumed as trial wave functions a linear combination of the exact solutions of the Hamiltonian of a hydrogen atom in the absence of magnetic fields.

The results obtained in this manner were reliable for magnetic fields ranging from 0 up to 10^9 G. In the same paper[1] a new trial wave function based on an expansion of the exact solution for the three-dimensional isotropic harmonic oscillator was proposed. This procedure is convenient for the study of the behavior of hydrogen (and hydrogenlike) atoms for fields up to on the order of 10^{11} G.

The present work has two main purposes: Firstly, we are interested to show that the same scheme, proposed in Ref. 1, can be used to study hydrogen atoms in magnetic fields ranging from 10^9 to 10^{11} G; it is only necessary to change the basis for the trial wave function. Secondly, we intend to verify which is the appropriate way to connect the energy levels obtained with the two different bases.

The Hamiltonian for the hydrogen atom in the presence of a uniform magnetic field in the $\hat{z}$ direction, in atomic units, i.e., energies in units of the Rydberg ($\mathcal{R}_\infty$) and lengths in units of the Bohr radius, is

$$H = -\nabla^2 - 2/r + \gamma L_z + \tfrac{1}{4}\gamma^2 r^2 \sin^2\theta\,, \tag{1}$$

where $\gamma = \mu_B \mathcal{H}/\mathcal{R}_\infty$ and L_z is the z component of the angular momentum operator.[1]

It is clear from Eq. (1) that the good quantum numbers are the parity and m (eigenvalue of L_z, in units of $\hbar$).

When $\gamma \simeq 1$ the magnetic energy is comparable with the electrostatic energy. In order to make a reasonable guess for the trial wave function, we recall that in the extreme limit ($\gamma \gg 1$) the problem is that of an electron in a magnetic field, which may be viewed as the superposition of a circular motion in the plane perpendicular to the magnetic field and of a free particle in the $\hat{z}$ direction. Therefore we may choose as a convenient basis set the eigenfunctions of the three-dimensional isotropic harmonic oscillator. When $\gamma \gg 1$, these eigenfunctions give a correct description of the electron in the xy plane while they fail in the z direction. In this way, we expect that this solution can give good results, compared to those of other authors,[2-9] for $1 \lesssim \gamma \lesssim 100$.

Therefore we may choose our trial wave function as

$$\Psi(\vec{r}) = \sum_i a_i \Phi_i(\vec{r}) \tag{2}$$

where the a_i's are variational parameters and Φ_i's are the eigenfunctions of the three-dimensional harmonic oscillator, which are given by

$$\begin{aligned}\Phi(\vec{r}) &= (2/r)^{1/2} \Lambda_k^{l+1/2}(r^2) Y_l^m(\theta, \phi) \\ &= Q_{nl}(r) Y_l^m(\theta, \phi)\,,\end{aligned} \tag{3}$$

with

$$k = \tfrac{1}{2}(n-l)\,, \quad n \geq l \geq 0 \tag{4}$$

(n and l must have the same parity) where

$$\Lambda_k^\alpha(t) = \left[\Gamma(\alpha+1)\binom{k+\alpha}{k}\right]^{-1/2} e^{-t/2} t^{\alpha/2} L_k^\alpha(t)\,, \tag{5}$$

with

$$\binom{p}{q} \equiv \frac{\Gamma(p+1)}{\Gamma(q+1)\Gamma(p-q+1)}\,, \tag{6}$$

and the $L_k^\alpha(t)$ are the Laguerre polynomials.

The functions given by Eq. (3) satisfy the Schrödinger equation

$$H_0 \Phi_i(\vec{r}) = \epsilon_i^{(0)} \Phi_i(\vec{r})\,, \tag{7}$$

where the Hamiltonian H_0 is given by (in appropriate units)

$$H_0 = -\nabla^2 + r^2 \tag{8}$$

and the eigenvalues are given by

$$\epsilon_i^{(0)} = 2(n + \tfrac{3}{2})\,. \tag{9}$$

Performing a change of variables in Eq. (1), and

remembering that $\sin^2\theta$ may be written as a linear combination of spherical harmonics, the Hamiltonian may be rewritten as

$$H = -\nabla^2 + r^2 + \sqrt{6}L_z - (\sqrt{6}/\gamma)^{1/2}(2/r) - (4\pi/45)^{1/2} r^2 Y_2^0(\theta, \phi). \quad (10)$$

For this Hamiltonian the energies are given in units of $(\gamma/\sqrt{6})\mathcal{R}_\infty$ and lengths in units of $(\sqrt{6}/\gamma)^{1/2}a_0$ (a_0 is the Bohr radius).

As suggested by Brandi,[1] using expansion (2) we calculate $\langle\psi|H|\psi\rangle$, which must be minimized with respect to the a_i's, subject to the constraint $\langle\psi|\psi\rangle = 1$.

This leads to the secular equation

$$\sum_j a_j[D_{kj} - (\eta_j - \epsilon_j)\delta_{kj}] = 0 \quad (11)$$

where η_j are the energy eigenvalues, ϵ_j is given by

$$\epsilon_j = \epsilon_j^{(0)} + \sqrt{6}m_j \quad (12)$$

and D_{kj} is an element of the symmetric matrix D and is given by

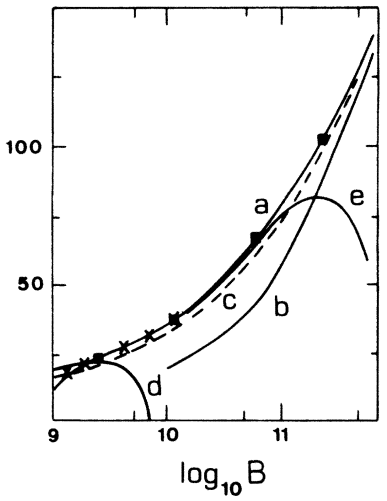

FIG. 1. Ionization energy of the ground state of hydrogen as a function of the magnetic field. Smith *et al.* (Ref. 6): a; Cohen *et al.* (Ref. 7): b; Wallis and Bowlden (Ref. 8): c; Brandi (Ref. 1): d; Larsen (Ref. 5): ■; Cabib *et al.* (Ref. 2): x; and present calculations: e.

$$D_{ij} = (-1)^{m_j+1}[(2l_i+1)(2l_j+1)]^{1/2} \times\left[2\left(\frac{\sqrt{6}}{\gamma}\right)^{1/2}\left\langle\frac{1}{r}\right\rangle_{ij}\delta_{l_i l_j}\begin{pmatrix} l_j & 0 & l_i \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_j & 0 & l_i \\ -m_j & 0 & m_i\end{pmatrix} + \langle r^2\rangle_{ij}\begin{pmatrix} l_j & 2 & l_i \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_j & 2 & l_i \\ -m_j & 0 & m_i\end{pmatrix}\right]. \quad (13)$$

TABLE I. Comparison between the present results (O), the results of Yafet *et al.*[9] (YKA), Larsen[5] (L), Praddaude[3] (P), Baldereschi and Bassani[4] (BBv and BBa), Cabib *et al.*[2] (CFF), and Brandi[1] (H) for the ground-state energy (units of rydbergs or effective rydbergs).

γ	YKA (Ref. 1)	L (Ref. 5)	P (Ref. 3)	BBv (Ref. 4)	BBa (Ref. 4)	CFF (Ref. 2)	H (Ref. 1)	O
0.1	−0.844 43	−0.995 05	−0.995 05	−0.995		−0.995 08	−0.995 04	−0.779 84
0.2	−0.839 56			−0.981		−0.980 76	−0.980 51	−0.855 43
0.3	−0.810 97	−0.958 35		−0.958		−0.958 41	−0.956 99	−0.870 78
0.4	−0.783 64			−0.927		−0.929 23	−0.924 82	−0.861 99
0.5	−0.750 54	−0.89		−0.890		−0.894 47	−0.884 06	−0.839 78
0.6	−0.712 52			−0.849		−0.854 94	−0.834 66	−0.808 75
0.7	−0.670 32	−0.81		−0.805		−0.811 42	−0.786 64	−0.771 34
0.8	−0.624 49			−0.758		−0.764 57	−0.709 88	−0.728 99
0.9	−0.575 54			−0.708		−0.714 73	−0.634 39	−0.682 68
1.0	−0.523 86	−0.662 17	−0.662 33	−0.655	−0.71	−0.662 41	−0.551 01	−0.633 08
1.5	−0.234 16	−0.37			−0.37	−0.370 76	−0.003 52	−0.349 81
2.0	0.091 90	−0.04	−0.044 42		−0.04	−0.044 50	−0.777 90	−0.027 59
2.5	0.441 92	−0.31			0.31	0.304 90	1.773 3	0.319 43
3.0	0.809 11	0.68	0.670 95		0.67	0.670 87	2.989 8	0.684 02
4.0	1.579 8				1.45	1.438 4	6.086 4	1.450 2
5.0	2.384 2	2.243 3			2.24	2.239 2	10.067	2.251 0

The quantities

$$\left\langle \frac{1}{r} \right\rangle_{ij} = \int_0^\infty Q_{n_j l_j} \frac{1}{r} Q_{n_i l_i} r^2 dr \tag{14}$$

and

$$\langle r^2 \rangle_{ij} = \int_0^\infty Q_{n_j l_j} r^2 Q_{n_i l_i} r^2 dr \tag{15}$$

may be calculated exactly in terms of Γ functions.

Therefore, as in Ref. 1, we have to diagonalize a symmetric matrix to obtain the eigenfunctions and energies for the Hamiltonian given by Eq. (10). This matrix also blocks along the diagonal because the Hamiltonian does not connect states of different symmetries (different m and parity). Hence for each block we obtain the energies and wave functions for states with definite m and parity. This fact enables us to study the numerical convergence of the energies corresponding to states with the same symmetry, independently of the states with other symmetry. The numerical convergence was checked by increasing the number of basis functions and comparing the results for the energy with those obtained using a more restricted basis.

In this way, in order to obtain the convergence of the ground state energy with five digits, up to $\gamma = 42.5$ ($\mathcal{H} \simeq 10^{11}$ G) we have included in our basis functions with $l = 0$ ($0 \leq n \leq 28$), $l = 2$ ($2 \leq n \leq 14$), $l = 4$ ($4 \leq n \leq 12$), $l = 6$ ($6 \leq n \leq 10$), $l = n = 8$, and $l = n = 10$. In a general way, to obtain the numerical convergence with four digits of the energies of the 14 lowest energy states, up to $\gamma = 42.5$, we had to include in our basis functions with $l = 0$ ($0 \leq n \leq 28$), $l = 1$ ($1 \leq n \leq 13$), $l = 2$ ($2 \leq n \leq 16$), $l = 3$ ($3 \leq n \leq 15$), $l = 4$ ($4 \leq n \leq 14$), $l = 5$ ($5 \leq n \leq 17$), $l = 6$ ($6 \leq n \leq 12$), $l = 7$ ($7 \leq n \leq 17$), $l = 9$ ($9 \leq n \leq 19$), and $l = 11$ ($11 \leq n \leq 17$).

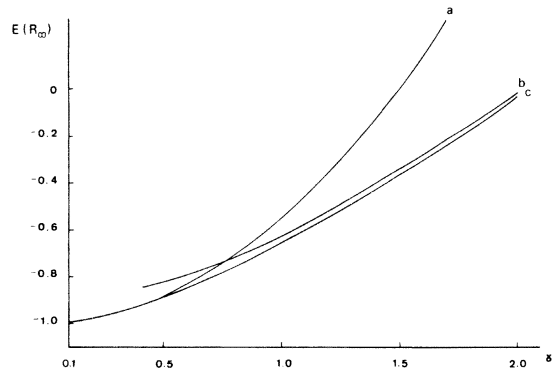

FIG. 2. Ground-state energy of the hydrogen atom in magnetic field as a function of γ. Brandi (Ref. 1): a; present work: b; and Cabib *et al.* (Ref. 2): c.

This scheme is still convenient to obtain the energies for hydrogen atoms in strong magnetic fields because of a fast numerical convergence (5 msec of central processor unit of an IBM 370/165 to obtain convergence up to four digits of the first four excited states).

Throughout this paper the labeling of the states of the hydrogen atom in the presence of a magnetic field is just an extension of that used in the absence of the field, for the good quantum numbers are m and parity.

Figure 1 compares results for the ionization energy of the ground state as a function of the magnetic field with those obtained by several authors. As discussed by Brandi,[1] we recall that the ionization energy of the ground state is given by

$$E_I = \gamma - E_{1s} \tag{16}$$

TABLE II. Comparison between the present results (O), the results of Larsen[5] (L), Praddaude[3] (P), Baldereschi and Bassani[4] (BBv and BBa), Cabib *et al.*[2] (CFF) and Brandi[1] (H) for the energy of the first excited state (units of rydbergs or effective rydbergs).

γ	L (Ref. 5)	P (Ref. 3)	BBv (Ref. 4)	BBa (Ref. 4)	CFF (Ref. 2)	H (Ref. 1)	O
0.1	−0.196 14	−0.196 17	−0.195 0		−0.196 2	−0.193 0	−0.153 0
0.2			−0.095 4		−0.097 9	−0.051 1	−0.073 2
0.3			0.006 7		0.003 3	0.172 3	0.019 6
0.4			0.104 0	0.127	0.101 7	0.480 9	0.116 5
0.5			0.200 6	0.217	0.198 4	0.876 2	0.216 4
0.6			0.296 7	0.310	0.294 5	1.358	0.318 9
0.7			0.392 7	0.404	0.390 5	1.929	0.423 5
0.8			0.488 9	0.498 5	0.486 5	2.586	0.530 1
0.9			0.585 4	0.592	0.582 8	3.332	0.638 5
1.0	0.683	0.678 97	0.682 1	0.687	0.679 3	4.165	0.748 3
1.5				1.169	1.163 6	9.647	1.314
2.0		1.651 94		1.657	1.651	17.32	1.902
2.5						27.18	2.503
3.0		2.634 63				39.24	3.116
4.0						69.94	4.363

where E_{1s} is the energy of the ground state of the hydrogen atom. From Fig. 1 we note that our results are in good agreement with those obtained by other authors for magnetic fields up to 10^{11} G, and they get worse thereafter. This should be expected, because, as mentioned before, this basis set describes exactly the motion of the xy plane, but it is only an approximation for the motion of the electron parallel to the magnetic field. It is clear then that the proposed basis will describe the system conveniently up to a certain value of γ.

In Table I we compare the present results for the ground-state energy with those obtained by other authors, for values of γ from 0.1 up to 5.0.

In Fig. 2 we show the energy of the ground state obtained by Brandi[1] and in the present work, as a function of γ, and it is seen that they are connected at $\gamma \simeq 0.76$. In this same figure we present the results obtained by Cabib *et al.*,[2] who integrated numerically the Schrödinger equation.

From Table I and Fig. 2 it is clear that for $\gamma < 0.76$ the values obtained for the ground-state energy are better when one uses the set of basis functions defined in Ref. 1; on the other hand, for $\gamma > 0.76$ the present basis functions give better results for the ground-state energy.

In Tables II and III we compare our results with those of several authors for the first 13 excited states. We verify that, in general, for $\gamma > 0.76$ the present results are in better agreement with those of Refs. 2–5, than the results obtained by Brandi.[1]

Hence, what we suggest is to use, within the same variational scheme, different trial wave functions for different regions of magnetic fields, in order to obtain the energy spectra.

As we have said, we are labeling the states as in the case of the H atom in the absence of magnetic field. In Tables I to III we have associated the levels obtained from our variational calculations with those of Brandi[1] using the noncrossing rule of Von Neumann and Wigner,[10] which states that levels with the same symmetry are not allowed to cross each other. When using the nodal surfaces criterion[11] there would not be agreement between the results at all and those of Refs. 3 and 5 (who did not have the problem of connection) for some excited states. For instance, the nodal-surfaces criterion would imply a larger energy for the $2s_0$ state than for the $3d_0$ state for large values of γ.[11] Detailed discussions about connecting low- and high-field spectra are presented for instance, in Refs. 2, 4, 11, and 12.

In Table IV we compare our results with those of Larsen.[5] The agreement is also good for $\gamma < 100$.

Unfortunately the results of Smith *et al.*[6] (which are the most accurate) for $\mathcal{H} > 10^9$ G are only avail-

TABLE III. Comparison between the present results (O) and the results of Praddaude[3] (P) and Brandi[1] (H) for some excited states (units of rydbergs or effective rydbergs).

	$\gamma = 0.1$			$\gamma = 1$			$\gamma = 2$			$\gamma = 3$		
	P	H	O	P	H	O	P	H	O	P	H	O
$2p_0$	−0.224 82	−0.223 4	−0.209 8	0.479 99	2.070	0.4813	1.404 61	9.005	1.413	2.359 96	20.56	2.385
$2p_{-1}$	−0.301 69	−0.322 9	−0.272 3	0.086 82	1.067	0.0920	0.800 83	6.995	0.804 6	1.592 97	17.54	1.597
$2p_{+1}$	−0.101 69	−0.122 9	−0.072 3	2.086 82	3.067	2.092 0	4.800 83	10.99	4.804	7.592 97	23.54	7.597
$3s$	−0.049 86	−0.024 5	−0.039 7	0.867 27	8.490	1.451	1.861 16	34.34	3.338	2.857 06	77.43	5.283
$3p_0$	−0.039 78	−0.027 1	−0.033 4	0.819 52	13.59	0.9308	1.806 12	54.72	2.166	2.789 69	123.2	3.457
$3p_{-1}$	−0.062 36	−0.070 1	−0.050 1	0.748 89	12.56	0.8244	1.714 92	52.59	1.955	2.694 61	119.9	3.136
$3p_{+1}$	−0.137 63	−0.129 8	0.149 8	2.748 89	14.56	2.824	5.714 92	56.59	5.955	8.694 61	125.9	9.136
$3d_0$	0.024 32	0.138 3	0.026 3	2.293 89	22.77	2.019	5.057 57	91.37	4.626	7.885 51	205.6	7.310
$3d_{-1}$	−0.115 62	−0.129 7	−0.113 8	0.586 86	21.47	0.6024	1.509 47	88.52	1.573	2.462 16	201.3	2.592
$3d_{+1}$	0.084 37	0.070 2	0.086 1	2.586 86	23.47	2.602	5.509 47	92.52	5.573	8.462 16	207.3	8.592
$3d_{-2}$	−0.175 67	−0.177 3	−0.172 6	0.293 89	20.52	0.2954	1.057 57	87.61	1.063	1.885 51	199.2	1.898
$3d_{+2}$	0.224 32	0.222 6	0.227 3	4.293 89	24.52	4.295	9.057 57	95.61	9.063	13.885 51	211.2	13.89

TABLE IV. Comparison between the present results (O) and the results of Larsen[5] (L) for the ground state and $2p_1$ state energies (units of rydbergs or effective rydbergs).

	$1s_0$		$2p_1$	
γ	L	O	L	O
5	2.243	2.251	13.28	13.15
25	20.267	23.677	71.81	71.98
100	92.543	99.871	294.7	300.2

able for the ground state, and we are not able to compare the present results with theirs for the excited states.

As a final comment we should note that a recent work of Glasser and Kaplan[13] shows that a non-relativistic treatment of hydrogen atoms in magnetic fields larger than 10^{10} G may be questioned.

We would like to thank Dr. L. C. M. Miranda for suggesting the problem.

*Work supported by Brazilian Agencies CAPES, FINEP and CNPq.

[1]H. S. Brandi, Phys. Rev. A 11, 1835 (1975).
[2]D. Cabib, E. Fabri, and G. Fiorio, Nuovo Cimento B 10, 185 (1972).
[3]H. C. Praddaude, Phys. Rev. A 6, 1321 (1972).
[4]A. Baldereschi and F. Bassani, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Keller *et al.* (U.S. Atomic Energy Commission, Oak Ridge, Tenn., 1970), p. 191.
[5]D. M. Larsen, J. Phys. Chem. Solids 29, 271 (1968).
[6]E. R. Smith, R. J. W. Henry, G. L. Surmelian, R. F. O'Connel, and A. K. Rajagopal, Phys. Rev. D 6, 3700 (1972).
[7]R. Cohen, J. Lodenquai, and M. Ruderman, Phys. Rev. Lett. 25, 467 (1970).
[8]R. Wallis and H. J. Bowlden, J. Phys. Chem. Solids 7, 78 (1958).
[9]Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids 1, 137 (1956).
[10]J. Von Neumann and E. P. Wigner, Phys. Z. 30, 467 (1929).
[11]R. J. Elliot and R. Loudon, J. Phys. Chem. Solids 15, 196 (1960).
[12]W. S. Boyle and R. E. Howard, J. Phys. Chem. Solids 19, 181 (1961).
[13]M. L. Glasser and J. I. Kaplan, Phys. Lett. 53A, 373 (1975).