Quadratic Zeeman effect for hydrogen: A method for rigorous bound-state error estimates

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We present a variational method, based on direct minimization of energy, for the calculation of eigenvalues and eigenfunctions of a hydrogen atom in a strong uniform magnetic field in the framework of the nonrelativistic theory (quadratic Zeeman effect). Using semiparabolic coordinates and a harmonic-oscillator basis, we show that it is possible to give rigorous error estimates for both eigenvalues and eigenfunctions by applying some results of Kato [Proc. Phys. Soc. Jpn. **4**, 334 (1949)]. The method can be applied in this simple form only to the lowest level of given angular momentum and parity, but it is also possible to apply it to any excited state by using the standard Rayleigh-Ritz diagonalization method. However, due to the particular basis, the method is expected to be more effective, the weaker the field and the smaller the excitation energy, while the results of Kato we have employed lead to good estimates only when the level spacing is not too small. We present a numerical application to the $m^p=0^+$ ground state and the lowest $m^p=1^-$ excited state, giving results that are among the most accurate in the literature for magnetic fields up to about 10^{10} G.

I. INTRODUCTION

In the last 20 years, the progress in Rydberg spectroscopy and, above all, the discovery in astrophysics of magnetic fields of intensity up to 10^{13} G have renewed the interest in the problem of quadratic Zeeman effect for the hydrogen atom, placed in a uniform magnetic field. An increasing number of both theoretical and experimental investigations have thus appeared on this subject and, in particular, a great computational effort has taken place (for a review, see Refs. 1–4) for the determination of the discrete spectrum of the Hamiltonian

$$H=-\tfrac{1}{2}\Delta-r^{-1}+\tfrac{1}{2}\gamma l_z+\tfrac{1}{8}\gamma^2(x^2+y^2)\ , \tag{1}$$

which is known[5] to be a widely applicable nonrelativistic approximation for our system. In Eq. (1), we have used atomic units $m_e=\hbar=e=1$, the magnetic field is given by $(0,0,\gamma)$ in units $(e/\hbar)^3 m_e^2 c=2.35\times10^9$ G, and l_z is the z component of the orbital angular momentum.

As a result of such a work, we have today a fairly complete knowledge of the spectrum of operator (1). Nevertheless, there is an aspect of the problem, which, in our opinion, deserves further attention, namely the rigorous error estimation for both eigenvalues and eigenfunctions. In fact, although there are in the literature highly accurate calculations, such as those of Ref. 2, a precise error estimation is given only in Refs. 1 and 4, but only for the ground-state energy. Here we would like to remind that a rigorous error determination has, first of all, a general motivation: the quadratic Zeeman effect in the hydrogen atom is, namely, one of the very few quantum-mechanical problems which is both physically meaningful and relatively simple and represents, therefore, a very interesting test for the application of classical results on error estimation.[6,7] We also remark that in our case a determination of the energy levels with an accurate error estimation can be useful, in view of the remarkable discrepancies of the results in the literature (see Tables I and II and Ref. 4) and that an estimate of the eigenfunction errors allows a reliable evaluation of quantities of direct physical interest, such as transition probabilities.

In the present paper we show that, making use of the so-called semiparabolic coordinates and introducing a harmonic-oscillator basis,[3,8] it is possible to formulate a variational method, exploiting Kato's results:[6] this leads to a determination of the discrete spectrum, giving, together with an upper bound to the eigenvalues, also a lower bound by means of Temple's formula and an eigenfunction error estimate by means of Kato's formula. Our method, however, has two limitations: the first one derives from the fact that we have used Kato's theory in its simplest form for nondegenerate levels, which, although valid for any self-adjoint operator whose spectrum satisfies certain conditions, is in practice the more effective, the larger the level spacing. The second limitation is related to our particular approach. We treat the quadratic magnetic term as a perturbation, in the sense that the basis functions of our variational method do not depend on the magnetic field strength γ; now, the effect of such a perturbation depends not only on γ, but also on properties of the unperturbed level. In fact, it is possible to evaluate an effective coupling constant, given roughly

TABLE I. Energies of the 0^+ ground state in units $\frac{1}{2}m_e e^4/\hbar^2$ (Rydberg units), as functions of magnetic field γ [in units $(e/\hbar)^3 m_e^2 c$], calculated by other authors.

γ	Ref. 16[a]	Ref. 21[a]	Ref. 22[a]	Ref. 23[a]	Ref. 5[a]	Ref. 24[b]
0.001						
0.1	−0.995 05	−0.995 04	−0.779 84	−0.9950		
0.6		−0.834 66	−0.808 75	−0.8348		
1	−0.662 33	−0.551 01	−0.633 08	−0.6620	−0.655[c]	
2	−0.044 42		0.319 43	−0.0439	−0.041[c]	−0.028 64
3	0.670 95		0.684 02			
10				6.5063		
20					15.5697	15.571 08
200					190.546	190.541 92
2000					1981.392	1981.4519

γ	Ref. 25[d]	Ref. 1[e]	Ref. 2[f]	Ref. 26[g]	Ref. 4[h]
0.001			−0.999 999		
0.1	−0.995 052 96		−0.995 053		
0.6			−0.854 925		
1	−0.661 233 72	−0.662 337 792(10)	−0.662 338		
2		−0.044 427 8(12)	−0.044 428	0.051	−0.044 427 6[i] −0.044 428 4[j]
3		0.670 932(10)	0.670 934	0.8422	
10		6.5044(4)	6.504 406	7.1784	
20		15.5694(22)	15.569 203	16.8222	15.569 35[i] 15.5691[j]
200		190.55(5)	190.5469	196.14	190.58[i] 190.52[j]
2000	1981.838 94	1981.4600(22)	1981.391 04	1996.1	

[a]Variational methods.
[b]Perturbation theory and finite difference technique.
[c]These are the values actually calculated. The author gives also better values, but obtained by extrapolation.
[d]Semiclassical perturbation theory.
[e]Perturbation theory and summation method. The authors give also a value with 20 exact figures.
[f]Numerical integration.
[g]Variational functionals.
[h]Moment method.
[i]Upper bound.
[j]Lower bound.

TABLE II. Energies of the lowest 1^- state calculated by other authors. Symbols and units are defined in Table I.

γ	Ref. 16[a]	Ref. 22[a]	Ref. 23[a]	Ref. 24[b]	Ref. 25[c]	Ref. 2[d]
0.001						−0.249 994 0
0.1	−0.201 69	−0.1723			−0.201 691 298	−0.201 691 3
0.6			0.4512			0.450 752 5
1	1.086 82	1.0928	1.0874		1.085 765 3	1.086 805 9
2	2.800 83	2.8046	2.8022	2.801 44		2.800 774
3	4.592 97	4.597				4.592 907
10			17.7519			17.749 155
20				37.069 08		37.069 05
200				393.3057		393.305 745
2000				3986.0964		3986.096 06

[a]Variational methods.
[b]Perturbation theory and finite difference technique.
[c]Semiclassical perturbation theory.
[d]Numerical integration.

by $\kappa=\gamma^2 n^4$, where n is the principal quantum number of the unperturbed level.[9]

In conclusion, our method is expected to give the more accurate results, the smaller κ and the larger the level spacing. In this first work, where our aim is to introduce the method, we present a numerical application, limited to the ground state and to the lowest excited state of angular momentum 1 and parity $-$, obtaining results which are among the best in the literature when κ does not exceed a few hundred.

II. DESCRIPTION OF THE METHOD

A. The variational problem

In Ref. 10 it has been shown that the use of the so-called semiparabolic coordinates

$$x=uv\cos\varphi,\quad y=uv\sin\varphi,\quad z=\tfrac{1}{2}(u^2-v^2)\ ,$$

$$u,v\geq 0,\ 0\leq\varphi\leq 2\pi\ ,$$

$$dx\,dy\,dz=(u^2+v^2)uv\,du\,dv\,d\varphi\ ,$$

in the problem of quadratic Zeeman effect is a very convenient method to introduce in an optimal way a basis of Sturmian type. Such bases are the more effective the smaller κ is and are very advantageous in order to estimate the error by the method presented in this work.

Remembering expression (1), the Schrödinger equation in coordinates (u,v) has the form

$$\frac{1}{2(u^2+v^2)}\left[\left[-\frac{\partial^2}{\partial u^2}-\frac{1}{u}\frac{\partial}{\partial u}+\frac{m^2}{u^2}+\omega u^2\right]+\left[-\frac{\partial^2}{\partial v^2}-\frac{1}{v}\frac{\partial}{\partial v}+\frac{m^2}{v^2}+\omega v^2\right]-4+(u^2+v^2)(\tfrac{1}{4}\gamma^2u^2v^2-\omega)\right]f(u,v)=Ef(u,v)\ , \quad (2)$$

where we denote by m the magnetic quantum number and omit, as usual, the constant energy $\frac{1}{2}\gamma m$; a term $\omega(u^2+v^2)$ has been added and subtracted, in order to produce the two operators in large parentheses, each representing the radial part of a plane harmonic-oscillator Hamiltonian with frequency $\sqrt{\omega}$ and angular momentum $l_z=m$ and acting, respectively, in the spaces $L^2(\mathbb{R}^+,u\,du)$ and $L^2(\mathbb{R}^+,v\,dv)$ [here, $L^2(W,ds)$ will denote the space of all functions on W, square integrable with respect to the measure s]. In Refs. 3 and 8, problem (2) has been solved by expanding f in a basis of harmonic oscillators of the mentioned type. Now, let us elucidate a basic point concerning the completeness of the basis: this will give us the occasion to justify some properties exploited in this work. Strictly speaking, problem (2) is formulated in the space $L^2(\mathbb{R}^{++},(u^2+v^2)uv\,du\,dv)$, with $\mathbb{R}^{++}=\mathbb{R}^+\times\mathbb{R}^+$, while the above harmonic-oscillator basis[11] is known to be complete in the space $L^2(\mathbb{R}^{++},uv\,du\,dv)$, as can be shown by well-known methods.[12] To prove that this is not a real difficulty, we first eliminate the term uv in both measures by means of the unitary transformation $(uv)^{1/2}f(u,v)=\psi(u,v)$: in this way, Eq. (2) can be written in the space $\mathcal{X}=L^2(\mathbb{R}^{++},(u^2+v^2)du\,dv)$ as

$$B^{-1}A\psi(u,v)=E\psi(u,v)\ , \quad (3)$$

where

$$B=2(u^2+v^2)\ ,$$

$$A=O_u+O_v-4+(u^2+v^2)(\tfrac{1}{4}\gamma^2u^2v^2-\omega)\ ,$$

$$O_u=-\frac{\partial^2}{\partial u^2}+(m^2-\tfrac{1}{4})\frac{1}{u^2}+\omega u^2\ ,$$

and O_v is obtained from O_u, substituting u by v. Here, O_u and O_v represent the two harmonic oscillators of Eq. (2) in spaces $L^2(\mathbb{R}^+,du)$ and $L^2(\mathbb{R}^+,dv)$. The operator $B^{-1}A$ is self-adjoint in the space $\mathcal{X}$, because it has been obtained form the operator (1), self-adjoint[13] in $L^2(\mathbb{R}^3,dx\,dy\,dz)$, by means of transformations which do not change this property. Also, the self-adjointness of $B^{-1}A$ implies that its domain D contains only functions which are regular as $u,v\to 0$. Remembering that the asymptotic behavior of functions belonging to space $\mathcal{X}$ is more restrictive than that required in the space $\mathcal{Y}=L^2(\mathbb{R}^{++},du\,dv)$, we deduce that

$$D\subset\mathcal{X}\cap\mathcal{Y}\ . \quad (4)$$

Denoting by $(\,|\,)$ and $\|\,\|$ the scalar product and norm of the space $\mathcal{X}$ and by $\langle\,|\,\rangle$ the scalar product of $\mathcal{Y}$, we have

$$(\psi|B^{-1}A\psi)=\tfrac{1}{2}\langle\psi|A\psi\rangle,\quad (\psi|\psi)=\tfrac{1}{2}\langle\psi|B\psi\rangle\quad\forall\psi\in D\ . \quad (5)$$

Relations (4) and (5) show that we can solve problem (3), given in the space $\mathcal{X}$, in the more convenient topology of the space $\mathcal{Y}$, expanding $\psi(u,v)$ in terms of a complete basis in the latter space, in particular, in terms of eigenfunctions of O_u and O_v.

In this paper we have preferred to apply an algorithm of direct minimization, instead of using the more usual Rayleigh-Ritz diagonalization, for the reasons explained below, in Sec. II C. In view of the use of this procedure, we prove now the equivalence of problem (3) to a minimum problem in $\mathcal{Y}$. The operator $B^{-1}A$ in Eq. (3) is self-adjoint in $\mathcal{X}$ and bounded from below.[14] Then, a well-known minimum principle holds for this eigenvalue problem.[7] Denoting by $E_0,E_1,\ldots$ $(E_0<E_1<\cdots)$ the eigenvalues of the operator $B^{-1}A$, here assumed to be

nondegenerate, and by $\psi_0, \psi_1, \ldots$ the corresponding eigenfunctions, we have

$$E_k = \min_{\psi \in D_k} \frac{(\psi | B^{-1} A \psi)}{(\psi | \psi)}, \quad k = 0, 1, 2, \ldots$$

where $D_0 = D$ and

$$D_k = \{\psi \in D : (\psi | \psi_i) = 0, \ i = 0, 1, \ldots, k-1\} , \quad k = 1, 2, \ldots .$$

Concerning our assumed nondegeneracy of the spectrum, we remind here that this is rigorously true[15] of E_0 for all values of γ, but we do not know comparable results for the other eigenvalues; nevertheless, there is a considerable numerical evidence (see Refs. 2 and 16) that at least a large part of the spectrum is nondegenerate, except some special values of γ (level-crossing points). In any case, the nondegeneracy of the spectrum is neither strictly necessary for the minimum principle[7] to hold, nor for the evaluation of error estimates,[6] but it only enables us to use Kato's theory in its simplest form.

Remembering Eq. (5), we can also write

$$E_k = \min_{\psi \in D_k} E(\psi), \quad k = 0, 1, 2, \ldots \tag{6}$$

where

$$E(\psi) = \frac{\langle \psi | A \psi \rangle}{\langle \psi | B \psi \rangle} , \tag{7}$$

which concludes our proof. Notice that the minimum problem (6) gives the whole discrete spectrum of given m. In this paper, we will select the domains D_k by working in subspaces of fixed m and parity p. We will also denote by ψ_{kN} the solution of (6) in a subspace spanned by the first N basis vectors, normalized as $\frac{1}{2}\langle \psi_{kN} | B \psi_{kN} \rangle = 1$, and by $E_{kN} = E(\psi_{kN})$, the corresponding energy.

B. Error estimates

Let H be a self-adjoint opertor in a Hilbert space $\mathcal{H}$, with scalar product and norm denoted by $(\ |\ )$ and $\|\ \|$; if H has nondegenerate discrete spectrum, such that $H\psi_i = \lambda_i \psi_i$, Kato[6] proved the following bounds for any λ_i:

$$\eta - \frac{\varepsilon^2}{\beta - \eta} \le \lambda_i \le \eta + \frac{\varepsilon^2}{\eta - \alpha} , \tag{8}$$

where $\eta = (\psi | H \psi)$, $\varepsilon = \|(H - \eta)\psi\|$, $\psi \in D(H)$, $\|\psi\| = 1$, and (α, β) is an open interval, such that $\varepsilon^2 < (\eta - \alpha)(\beta - \eta)$, containing the only spectral point λ_i. Kato also proved the inequality

$$1 - |(\psi | \psi_i)|^2 \le [(\eta - \tfrac{1}{2}(\alpha + \beta))^2 + \varepsilon^2][\tfrac{1}{2}(\beta - \alpha)]^{-2} , \tag{9}$$

where $\|\psi_i\| = 1$.

In view of the fact that the operator $B^{-1}A$ is self-adjoint in the space $\mathcal{X}$ and we can assume it has a nondegenerate discrete spectrum, Kato's results can be applied very simply to problem (3) setting $\mathcal{H} = \mathcal{X}$, $H = B^{-1}A$, and $\lambda_i = E_i$. From Eq. (5) we find $\|\psi_{iN}\| = 1$,

$$(\psi_{iN} | B^{-1} A \psi_{iN}) = \tfrac{1}{2}\langle \psi_{iN} | A \psi_{iN} \rangle = E_{iN} ,$$

$$\|(B^{-1}A - E_{iN})\psi_{iN}\|^2 = \tfrac{1}{2}\langle (A - E_{iN}B)\psi_{iN} | B^{-1}(A - E_{iN}B)\psi_{iN} \rangle \equiv \Delta^2 . \tag{10}$$

Thus, introducing in the first inequality (8) $\psi = \psi_{iN}$, $\eta = E_{iN}$, and $\varepsilon = \Delta$, we get for each eigenvalue E_i

$$E_{iN} - \frac{\Delta^2}{\beta - E_{iN}} \le E_i, \quad i = 0, 1, \ldots \tag{11}$$

which is the well-known Temple formula. In the case of the lowest state we can choose $\alpha = -\infty$ and β such that $E_0 < \beta \le E_1$.

Concerning the estimate of the eigenfunction error, we observe that in the present paper we calculate only the lowest states of given m and p; in this case the bound in the right-hand side of (9) can be replaced[6] by the more precise one, $\varepsilon^2[(\beta - \eta)^2 + \varepsilon^2]^{-1}$. Defining

$$F_{iN}^2 \equiv 1 - |(\psi_{iN} | \psi_i)|^2 , \tag{12}$$

the inequality (9) becomes

$$F_{iN}^2 \le \frac{\Delta^2}{(\beta - E_{iN})^2 + \Delta^2} \equiv \sigma_{iN}^2 , \tag{13}$$

which is Kato's formula. A meaningful expression for F_{iN} is easily found to be $F_{iN}^2 = \|\psi_{iN} - \psi_i\|^2 - \frac{1}{4}\|\psi_{iN} - \psi_i\|^4$. The quantity σ_{iN} is a convenient estimate of the eigenfunction error; $\sigma_{iN} = 0$ implies an exact eigenfunction; $\sigma_{iN} = 1$ implies $\beta = E_{iN}$, so that formula (11) becomes useless and from (12) and (13) we see that a calculated eigenfunction orthogonal to the exact one cannot be ruled out. It is worthwhile remarking that when the levels E_i and E_{i+1} are almost degenerate, σ_{iN} is very close to 1, since $E_i < \beta \le E_{i+1}$, so that the estimates (11) and (13) are rather bad, even if Δ is not very large.

C. The algorithm

We conclude this section by describing the structure of our algorithm. For each state, identified by angular momentum projection m, parity p, and energy $E_i^{(m,p)}$, we introduce (see also Refs. 3 and 8) as a basis set the symmetric or the antisymmetric products of the normalized eigenfunctions of the two operators O_u and O_v, optimizing numerically the values of the oscillator parameter ω for each choice of the magnetic field γ. This basis has two advantages, which are shared by all other Sturmian bases described in Ref. 10. The first is that the calculation of all matrix elements involved can be carried out analytically: it is straightforward for the operators A and B and is not particularly difficult for B^{-1}. The second advantage is that the matrices corresponding to A and B have a band structure, which is essential for our error estimation, as explained below.

We minimize directly the functional (7) in finite dimensional subspaces by means of a sequence of one-dimensional minimization steps (iterations) along the so-called conjugate directions.[17] This method has the gen-

eral limitation that it can be easily applied only to the lowest level of given m and p, the calculation of higher levels requiring orthogonality conditions to previously calculated eigenfunctions; compared with the standard Rayleigh-Ritz method with the same basis, it has better numerical precision and stability, is of simpler implementation in a computer, and, what is most important, saves storage space and computing time, avoiding complicated operations with large matrices (see also Ref. 18). On the other hand, the computation of any excited state is more manageable by means of the Rayleigh-Ritz method. Since in this paper we deal only with the two lowest 0^+ and 1^- levels, the direct minimization method has been preferred.

We calculate the quantities Δ, defined in Eq. (10), and $\Delta_N = \|[(B^{-1}A)_N - E_{iN}]\psi_{iN}\|$, where $(B^{-1}A)_N$ is the $N \times N$ matrix, projected from the corresponding operator. These quantities represent the root-mean-square energy deviations for the exact and the truncated operators, so that $\Delta \geq \Delta_N$. As we have seen, the knowledge of Δ is important because it determines through Temple's and Kato's inequalities (11) and (13) our error estimate for any eigenvalue and eigenfunction. The constant β in these inequalities must satisfy $E_{iN} < \beta \leq E_{i+1}$ and has been chosen here as the value of E_{i+1} given in Ref. 2. In general, the calculation of Δ is not so simple, due to the fact that one should have a good criterion to truncate the infinite sums involved. In the case of our basis, such a criterion is automatically provided by the band structure of the matrix A_N, namely, $A_{Nij} = 0$ for $|i-j| > c(N)$ $(i,j = 1, \ldots N)$, where c is an increasing function of N, and by an analogous structure of the matrix representing B. It is easily seen that, although B^{-1} has not such property, the calculation of Δ becomes exact if we include in the summation implied by Eq. (10) all index values up to a certain $M(N) > N$. As an empirical rule, we have found $M(20) = 34$, $M(40) = 60$, $M(60) = 84$, $M(80) = 108$, $M(100) = 130$, and $M(150) = 186$.

In virtue of the equivalence of the minimum problem (6) and Eq. (3), the smallness of Δ_N is related to the precision of the solution of problem (6) in the N-dimensional subspace: $\Delta_N = 0$ means that this solution has been reached. Therefore, the condition $\Delta_N \leq 10^{-6}$ has been used to stop our iterations; when the convergence is too slow, as in the cases $\gamma \geq 200$, other criteria are needed for this purpose. An interesting test is given by the evaluation of the positive number $\delta = \Delta/\Delta_N - 1$, which tends in general to infinity as the iteration converges to the solution: it turns out that the smaller δ at a given iteration, the faster the rate of convergence. A small value of δ at the beginning indicates a good value of the basis parameter ω.

TABLE III. Energies of the 0^+ ground state and of the lowest 1^- state calculated in the present paper. Upper bounds are calculated by the variational method described in the text; lower bounds by Temple's formula. Eigenfunction error estimate σ [Eq. (13)] is also given.

Magnetic field γ	Lowest 0^+ state (ground state) Upper bound / Lower bound	σ [Eq. (13)]	Lowest 1^- state Upper bound / Lower bound	σ [Eq. (13)]
0.001	−0.999 999 500 000 552 −0.999 999 500 000 553	2.73×10^{-8}	−0.249 994 000 231 967 −0.249 994 000 231 968	7.03×10^{-8}
0.1	−0.995 052 960 802 18 −0.995 052 960 802 20	1.74×10^{-7}	−0.201 691 344 745 7 −0.201 691 344 749 2	3.84×10^{-6}
0.6	−0.854 924 557 551 0 −0.854 924 557 553 5	4.60×10^{-6}	0.450 752 454 4 0.450 752 451 8	7.04×10^{-5}
1	−0.662 337 793 3 −0.662 337 794 5	2.90×10^{-5}	1.086 805 88 1.086 805 79	3.75×10^{-4}
2	−0.044 427 815 −0.044 427 820	5.77×10^{-5}	2.800 774 2.800 767	2.69×10^{-3}
3	0.670 934 02 0.670 933 86	2.84×10^{-4}	4.592 906 90 4.592 902 27	2.05×10^{-3}
10	6.504 405 6.504 388	2.35×10^{-3}	17.749 17 17.747 47	2.99×10^{-2}
20	15.569 209 15.568 175	1.61×10^{-2}	37.069 21 37.037 32	1.11×10^{-1}
200[a]	190.57 185.12	0.624	393.46 389.05	0.666
2000[a]	1985.35 1681.06	0.983	3993.33 −6480	0.999 97

[a]Upper and lower bounds are calculated for different wave functions. σ corresponds to the lower bound.

III. NUMERICAL RESULTS

In Table III we report our results for the ground state ($m=0$, $p=1$) and for the lowest $|m|=1$, $p=-1$ state: for each value of the magnetic field γ we give the variational upper bound and Temple's lower bound to the energy, as well as Kato's upper bound to eigenfunctions error, given by σ_{iN}, Eq. (13). The dimension of the employed subspace has been increased with γ, from $N=20$ up to $N=150$.

In Table IV we give for the ground state the same quantities as in Table III, for a fixed magnetic field ($\gamma=2$), as functions of the subspace dimension N.

Our results are very satisfactory in the weak field and low excitation region, namely for values of the effective coupling constant κ up to values of a few hundred (here, $n=1$ for the 0^+ state, $n=2$ for 1^-). A comparison of our data in Tables III and IV with those of other authors in Tables I and II shows that our energies are the best, in the range $\gamma \leq 20$ for the ground state and $\gamma \leq 3$ for the 1^- state, except one case, not reported in the tables. The exception is a result of Ref. 1, where the ground-state energy for $\gamma=0.2$ is given with 20 exact figures, which should compare with 13 exact figures obtained by us, with $N=40$; we believe, however, that this difference in performance is due essentially to the precision used in our actual calculation. Of course, in the same cases, also our eigenfunctions are expected to be the best ones, although no direct comparison is possible. However, for the reasons mentioned in the Introduction, it is evident that our precision deteriorates with increasing κ. For $\gamma=0.001=2.35\times10^6$ G the relative errors in energy, computed from our upper and lower bounds, are of the order of 10^{-15} for both levels, while the eigenfunction error estimates σ_{iN}, of the order 10^{-8}, show a different behavior for the two levels. For $\gamma=20=4.7\times10^{10}$ G, the analogous errors are 6×10^{-5} and 8×10^{-4} for the two energies, 0.016 and 0.11 for the wave functions. For $\gamma=2000=4.7\times10^{12}$ G the energy values are still reasonably good, since our upper bounds, compared with the more precise values of Ref. 2, have a discrepancy of about 0.2%; on the other hand, the quantity σ_{iN} is almost equal to 1, which means that the calculated wave functions and Temple's lower bounds are bad, and this is especially true of the 1^- state.

TABLE IV. The same as in Table III, for the ground state, fixed $\gamma=2$, as functions of the subspace dimension N.

N	Upper bound Lower bound	σ_N [Eq. (13)]
20	−0.044 185 8 −0.058 406 1	9.12×10^{-2}
40	−0.044 426 6 −0.044 455 4	4.12×10^{-3}
60	−0.044 427 78 −0.044 428 57	6.80×10^{-4}
80	−0.044 427 813 −0.044 427 934	2.67×10^{-4}
100	−0.044 427 815 2 −0.044 427 820 8	5.77×10^{-5}
150	−0.044 427 815 328 −0.044 427 815 424	7.50×10^{-6}

IV. CONCLUSIONS

By applying the classical results of Ref. 6, we have shown that for the nonrelativistic problem of the hydrogen atom in a strong uniform magnetic field a calculation is possible with a rigorous error estimate of both eigenvalues and eigenfunctions. The essential difficulty in computing such estimates is the exact evaluation of the quantity Δ [Eq. (10)] appearing in Temple's and Kato's formulas, or at least of an upper bound to it. We were able to perform an exact evaluation of this quantity by exploiting the band structure of the involved operators, resulting from the use of semiparabolic coordinates and harmonic-oscillator basis.

We note that to the above advantage of our method, there corresponds the limitation that it is less effective the larger the effective coupling constant κ: this means larger magnetic field and excitation energy. The precision of the lower bounds is also affected by the level spacing in the chosen (m,p) subspace, since we have used Kato's theory for nondegenerate levels. Our application to the lowest 0^+ and 1^- levels indicates that the method is highly efficient up to κ values of the order of a few hundred. The application to all excited states of a given (m,p) subspace, within the mentioned limits, is still possible, but in this case the Rayleigh-Ritz diagonalization should be preferred to our algorithm of direct minimization. Apart from an obvious recourse to a larger dimension, extensions of our method to larger values of κ can, possibly, be found in modifications of our variational approach; on the other hand, in the case of a too-small level spacing, the exploitation of the more general form of Kato's[6] estimates, valid for degenerate or almost-degenerate levels, should be advantageous. Concerning the modifications of the variational approach, we can suggest a more sophisticated determination of ω (for instance, of the type discussed in Ref. 19) and the use of a γ-dependent basis, allowing for the increase of κ. In this respect, one might be tempted to consider the variational approach of Ref. 5, where the use of cylindrical coordinates makes it possible to consider the Coulomb interaction as a perturbation. Although such an approach is complementary to ours, in the sense that the best results are obtained for the largest magnetic fields, nevertheless it makes the calculation of Δ more difficult. In this case, indeed, the matrices of the operators A and B, whose elements should be computed numerically, no longer have a band structure. Concerning the theory of Kato in the case of degenerate or almost degenerate levels, we remark that Ref. 6 gives only expressions of lower bounds to energy levels; however it is not difficult to obtain in this case formulas analogous to (9) or (13) for eigenfunctions errors.

Finally, one should keep in mind the physical limita-

tion of our work, remembering that the relativistic corrections become increasingly important as κ grows[20] and, for the highest values we have considered, where the energy of the levels amounts to about one tenth of the electron rest energy, they may be comparable with the numerical uncertainties.

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