Quadratic Zeeman effect in hydrogen Rydberg states: Rigorous error estimates for energy eigenvalues, energy eigenfunctions, and oscillator strengths

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(Received 23 March 1994)

A variational method, based on some results due to T. Kato [Proc. Phys. Soc. Jpn. **4**, 334 (1949)] and previously discussed, is here applied to the hydrogen atom in uniform magnetic fields of a few tesla in order to calculate, with a rigorous error estimate, energy eigenvalues, energy eigenfunctions, and oscillator strengths relative to Rydberg states up to just below the field-free ionization threshold. Making use of a basis (parabolic Sturmian basis) with a size varying from 990 up to 5050, we obtain, over the energy range of -190 to -24 cm^{-1}, all of the eigenvalues and a good part of the oscillator strengths with a remarkable accuracy. This, however, decreases with increasing excitation energy and, thus, above ~ -24 cm^{-1}, we obtain results of good accuracy only for eigenvalues ranging up to ~ -12 cm^{-1}.

PACS number(s): 32.60.+i, 32.80.Rm, 02.90.+p

I. INTRODUCTION

The rapid progress of high-resolution laser spectroscopy and the investigation of the so-called "quantum chaos" have recently stimulated a great deal of work on diamagnetic Rydberg states of the hydrogen atom in uniform magnetic fields of a few tesla. At present, the results obtained [1–3] cover the whole region of the highly excited discrete spectrum and the adjacent continuum. These results represent the most complete description of a quantum system ever made and are rightly considered [4] a spectacular confirmation of quantum theory. With reference to this latter context, it seems to us, however, rather surprising that the various authors have not given any particular emphasis to the evaluation of rigorous error estimates for each of the calculated quantities and that the agreement with the experimental results is normally shown by making use only of graphics. Although this procedure of comparing theoretical with experimental values can be partially understood, for the plenty of the data taken into account, nevertheless, the absence of any quotation of numerical values makes the quantitative aspect of the comparison somewhat vague.

In the present paper, we carry out again, but with a larger and more rigorous accuracy, part of calculations which in Ref. [2] were compared with the experiments. Our results are obtained by pushing, up to Rydberg states shortly below the field-free ionization threshold ($E = 0$), the error method described in works [5,6]. This method is based essentially on some results due to Kato [7] and it provides error estimates for energy eigenvalues, energy eigenfunctions, and oscillator strengths. The error estimates for eigenvalues are determined by evaluating Rayleigh-Ritz upper bounds and generalized Temple's lower bounds. The error estimates for eigenfunctions are given by some formulas (Kato's formulas), whereas the error estimates for oscillator strengths are obtained through upper and lower bounds, which are derived in the present paper as a consequence of Kato's results.

II. ERROR-ESTIMATE METHOD

In this section, we confine ourselves to give only a brief account of the mathematical setting of our method and of the consequent error formulas both for eigenvalues and eigenfunctions. A complete treatment of these arguments as well as an exhaustive description of the performance of the method can be found in papers [5,6]. We discuss, instead, in detail the point concerning the error bounds for oscillator strengths.

On introducing the "semiparabolic coordinates" $u = (r+z)^{1/2}$, $v = (r-z)^{1/2}$, and $\varphi = \tan^{-1}(y/x)$, separating out the angular φ motion, and subtracting the linear Zeeman shift, the Schrödinger equation for the hydrogen atom in a uniform magnetic field lying along the z axis can be written in the two following equivalent forms: the eigenvalue problem

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

in the space $L^2(\mathbb{R}^{++}, (u^2+v^2)\,du\,dv)$ and the generalized eigenvalue problem

$$A\psi(u,v) = EB\psi(u,v) \tag{2}$$

in the space $L^2(\mathbb{R}^{++}, du\,dv)$ [8], with, in both cases,

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

and

$$A = \left[-\frac{\partial^2}{\partial u^2} + \left(m^2 - \frac{1}{4}\right)\frac{1}{u^2} + \omega u^2\right] + \left[-\frac{\partial^2}{\partial v^2} + \left(m^2 - \frac{1}{4}\right)\frac{1}{v^2} + \omega v^2\right] - 4 + \left(u^2+v^2\right)\left(\frac{1}{4}\gamma^2 u^2 v^2 - \omega\right).$$

Notice that the proton mass has been assumed infinite and that the Rydberg unit of energy and the atomic units $m_e = \hbar = e = 1$ have been used. Also, m denotes the magnetic quantum number, ω is a nonlinear variational parameter, and γ denotes the magnetic field measured in units of $(e/\hbar)^3 m_e^2 c \simeq 2.35 \times 10^9$ G. Both the equations above play a precise role in our method. We find Eq. (2) convenient for the evaluation of approximate eigenfunctions and of upper bounds to the exact eigenvalues E_i, $i = 0, 1, 2, \ldots$. This equation, in fact, permits the application of the Rayleigh-Ritz (RR) method with a basis (parabolic Sturmian basis) [6], which is simple, efficient, orthonormal, and complete according to the topology of $L^2(\mathbb{R}^{++}, du\,dv)$. In order to derive lower bounds to eigenvalues and error estimates for eigenfunctions, it is instead necessary to refer to Eq. (1). Let us now introduce the following notation. $(\,|\,)$ and $\|\ \|$ are the scalar product and norm of the space $L^2(\mathbb{R}^{++}, (u^2+v^2)\,du\,dv)$. $\langle\,|\,\rangle$ and $|\ |$ are the scalar product and norm of the space $L^2(\mathbb{R}^{++}, du\,dv)$. The symbol $|\ |$ will denote also the norm of matrices in Sec. III. ψ_{iN} is the normalized ($\|\psi_{iN}\| = 1$) approximate eigenfunction corresponding to the exact eigenvalue E_i, obtained by the RR method applied to Eq. (2) in an N-dimensional subspace. A_N, B_N, and B_N^{-1} are the $N \times N$ matrices corresponding to the operators A, B, and B^{-1}. $B^{-1}_{N,N'}$ is the $N \times N'$ matrix corresponding to the operator B^{-1}. $E_{iN} = (\psi_{iN}|B^{-1}A\psi_{iN})$ is the expectation value of the energy. $\Delta_{iN} = \|(B^{-1}A - E_{iN})\psi_{iN}\|$ is the root-mean-square energy deviation. $W_{iN} = E_{iN} - \Delta_{iN}$ is Weinstein's lower bound. $\delta_{iN} = \Delta_{iN}^2/(W_{i+1,N} - E_{iN})$. $T_{iN} = E_{iN} - \delta_{iN}$ is Temple's lower bound. $\eta_{iN} = (E_{i-1,N} + W_{i+1,N})/2$. Notice (see Refs. [5,6]) that the quantities E_{iN} and Δ_{iN} can be also written as

$$E_{iN} = \langle \psi_{iN} | A \psi_{iN} \rangle \tag{3}$$

and

$$\Delta_{iN} = \langle (A - E_{iN}B)\psi_{iN} | B^{-1}(A - E_{iN}B)\psi_{iN} \rangle^{1/2} \tag{4}$$

and that, to within the numerical accuracy of our calculations, E_{iN} can be identified with the RR eigenvalue. Taking into account this fact and the result that the RR eigenvalues are upper bounds to the corresponding exact eigenvalues E_i (Poincaré's theorem, see Ref. [6]), we have here

$$E_{iN} \geq E_i \quad , \quad i = 0, 1, 2, \ldots \ . \tag{5}$$

Furthermore, we assume that our RR procedure is convergent, i.e.,

$$E_{iN} \longrightarrow E_i \ , \quad \Delta_{iN} \longrightarrow 0 \quad \text{as} \quad N \longrightarrow \infty. \tag{6}$$

Making use of (5) and (6) and the self-adjointness of the operator $B^{-1}A$ in the space $L^2(\mathbb{R}^{++}, (u^2+v^2)\,du\,dv)$, we find [6] that the half-closed interval $(W_{iN}, E_{iN}]$ contains the sole eigenvalue E_i, if N is high enough to satisfy the conditions

$$\Delta_{iN} < (E_{i+1} - E_i)/2 \ , \quad \Delta_{iN} \leq E_i - E_{i-1} \tag{7}$$

(when $i = 0$ we can set $E_{-1} = -\infty$). In other words, we have the estimate (Weinstein's formula)

$$W_{iN} < E_i \leq E_{iN}. \tag{8}$$

If, in addition, $W_{i+1,N}$ is a lower bound to E_{i+1} and

$$W_{i+1,N} > E_{iN} + \Delta_{iN} \ , \quad E_{i-1,N} \leq W_{iN}, \tag{9}$$

we get the more accurate estimate (generalized Temple's formula)

$$T_{iN} \leq E_i \leq E_{iN}. \tag{10}$$

In order to estimate the eigenfunction error, let us consider the quantity $F_{iN} = [1 - |(\psi_{iN}|\psi_i)|^2]^{1/2}$, where ψ_i denotes the exact eigenfunction corresponding to the eigenvalue E_i and $\|\psi_{iN}\| = \|\psi_i\| = 1$. The quantity F_{iN} is indeed a convenient measure of the eigenfunction error because

$$F_{iN}^2 = \|\psi_{iN} - \psi_i\|^2 - \frac{1}{4}\|\psi_{iN} - \psi_i\|^4. \tag{11}$$

Estimates for this quantity are given by Kato's formulas [7]. Making use again of the self-adjointness of $B^{-1}A$ and assuming that all the conditions necessary to deduce (10) are satisfied, the first Kato formula in our notation is written

$$F_{iN}^2 \leq \frac{(E_{iN} - \eta_{iN})^2 + \Delta_{iN}^2}{[(W_{i+1,N} - E_{i-1,N})/2]^2} \equiv \sigma_{i(1)}^2. \tag{12}$$

If in addition either $E_{iN} \leq \eta_{iN}$ or $E_{iN} \geq \eta_{iN} + \delta_{iN}$, we have, respectively, the more accurate formulas

$$F_{iN}^2 \leq \frac{\Delta_{iN}^2}{(E_{iN} - E_{i-1,N})(W_{i+1,N} - E_{iN})} \equiv \sigma_{i(2)}^2 \tag{13}$$

and

$$F_{iN}^2 \leq \frac{\Delta_{iN}^2}{(W_{i+1,N} - E_{iN})^2 + \Delta_{iN}^2} \equiv \sigma_{i(3)}^2. \tag{14}$$

It should be observed that estimate (13) is actually a slight improvement of the corresponding estimate given by Kato. It is obtained simply by making use of condition (5) in the original Kato derivation. We also point out that, when our method yields only Weinstein's lower bounds, estimate (14) becomes impossible and we cannot have estimates (12) and (13) better than the useless ones $\sigma_{i(1)} = \sigma_{i(2)} = 1$.

We now turn our attention to the derivation of upper and lower bounds on oscillator strengths. For the sake of brevity, we consider in detail only the case which concerns the present paper, i.e., the case of the oscillator strengths f_i relative to $\Delta m = 0$ Balmer transitions to $m = 0$ even-parity Rydberg states. In the units previously mentioned and recalling that the space $L^2(\mathbb{R}^{++}, (u^2+v^2)\,du\,dv)$ is real, we have [9]

$$f_i = (E_i - E_1)(\psi_1|z\,\psi_i)^2, \tag{15}$$

where $z = \frac{1}{2}(u^2 - v^2)$ and ψ_1 ($\|\psi_1\| = 1$) is the exact $m = 0$ odd-parity eigenfunction corresponding to the

eigenvalue E_1, whereas ψ_i ($\|\psi_i\| = 1$) is the generic $m = 0$ exact Rydberg eigenfunction associated with the eigenvalue E_i and having positive parity. In order to find out upper and lower bounds to f_i, we first need to determine an estimate for the quantity

$$|(\psi_1|z\,\psi_i) - (\psi_{1N}|z\,\psi_{iN})|, \tag{16}$$

where ψ_{1N}, ψ_{iN} ($\|\psi_{1N}\| = \|\psi_{iN}\| = 1$) are the approximate RR eigenfunctions to ψ_1 and ψ_i, respectively. The finding of this estimate becomes easier if one sets $\psi_1 = \psi_{1N}$. When γ takes on laboratory values (as in the present paper), ψ_1 is usually identified (see, for example, Ref. [1]) with the corresponding unperturbed hydrogenic eigenfunction Ψ_1. In so doing, one has obviously $\psi_1 = \psi_{1N} = \Psi_1$. This procedure is (as we shall see in Sec. IV) an excellent approximation. However, here, given our rigor purposes, we have preferred the more rigorous way of computing ψ_{1N} and of setting then $\psi_1 = \psi_{1N}$. Indeed, since our method is more effective for low-lying states, we have found that our ψ_{1N} is practically the exact eigenfunction ψ_1 (error $\sigma_{(2)}$ of order 10^{-26}). Assuming thus from now on $\psi_1 = \psi_{1N}$ in (16), we get immediately the estimate

$$|(\psi_1|z\,\psi_i) - (\psi_1|z\,\psi_{iN})| \le \|z\,\psi_1\|\;\|\psi_i - \psi_{iN}\|,$$

making use only of the Schwarz inequality and the self-adjointness of z. Denoting by ζ the value of the quantity $\|z\psi_1\|$ [10] and taking account of the inequality

$$\|\psi_i - \psi_{iN}\| \le \left(2 - 2\sqrt{1-\sigma_{i(\cdot)}^2}\right)^{1/2} \equiv \Sigma_i$$

($\sigma_{i(\cdot)} = \sigma_{i(1)}, \sigma_{i(2)}, \sigma_{i(3)}$), which easily follows from (11)–(14) assuming $(\psi_i|\psi_{iN}) \ge 0$, we get the new estimate

$$(\psi_1|z\,\psi_{iN}) - \zeta\Sigma_i \le (\psi_1|z\,\psi_i) \le (\psi_1|z\,\psi_{iN}) + \zeta\Sigma_i.$$

TABLE I. Column 1 (i): indices numbering the states $m^p = 0^+$ according to decreasing binding energy; column 2 (Δ): root-mean-square energy deviations [Eq. (4)]; column 3 (σ): eigenfunction-error estimates $\sigma_{i(1)}, \sigma_{i(2)}$, and $\sigma_{i(3)}$ [formulas (12)–(14)] according to the index in parentheses; column 4 ($-E_l^u$): upper (u) and lower (l) bounds on the eigenvalues E_i with sign changed and in units of 10^{-3} Ry; column 5 (f_l^u): upper (u) and lower (l) bounds (in units of 10^{-5}) on the oscillator strengths relative to the $\Delta m = 0$ transitions $E_1 \to E_i$. Notice that the lower-bound digits are reported starting from where upper- and lower-bound digits begin to be different. Thus a single value in column $-E_l^u$ means that upper and lower bounds coincide. All the energy lower bounds are Temple's [formula (10)], the dimension of the subspace is $N = 990$, $\gamma = 2.55 \times 10^5$, and the energy interval (in cm^{-1}) filled by the results is $I = -189.99$ to -176.94.

i	Δ (Ry)	σ	$-E_l^u$	f_l^u
144	1.2×10^{-18}	1.4×10^{-13} (3)	1.731 336 789 335 240 221 306 24	6.443 519 062 783 18520
145	5.9×10^{-19}	8.0×10^{-14} (3)	1.722 719 902 236 339 176 518 41	4.724 239 485 6417 1783
146	6.6×10^{-19}	1.1×10^{-13} (3)	1.715 376 240 561 938 255 546 64	3.325 254 963 3795 28504
147	5.3×10^{-19}	8.7×10^{-14} (2)	1.709 330 777 244 665 495 517 40	2.470 371 780 3461 799821
148	1.1×10^{-18}	1.6×10^{-13} (2)	1.703 168 814 819 053 515 567 78	2.533 772 739 9931 3295
149	9.8×10^{-19}	1.1×10^{-13} (2)	1.695 337 785 375 935 474 162 34	2.533 646 673 6351 1554
150	9.6×10^{-19}	9.2×10^{-14} (2)	1.685 725 763 428 141 706 856 31	2.152 235 841 5901 2305
151	1.4×10^{-18}	1.1×10^{-13} (2)	1.674 413 523 110 981 916 406 85	1.480 914 550 2986 499344
152	1.0×10^{-18}	7.5×10^{-14} (2)	1.661 429 436 070 235 009 018 15	0.679 398 237 57641 41130
153	1.7×10^{-18}	1.1×10^{-13} (2)	1.646 778 374 139 312 119 779 03	0.061 221 173 455467 381646
154	1.2×10^{-18}	7.1×10^{-14} (2)	1.630 454 041 816 919 955 913 56	0.388 875 861 08939 097063
155	2.6×10^{-19}	1.5×10^{-14} (3)	1.612 443 761 400 359 460 218 21	5.674 623 074 0667 39731

The required upper and lower bounds for f_i are now obtained simply by making use of (10). We thus find

$$f_i^l \le f_i \le f_i^u,$$

where

$$f_i^u = (E_{iN} - E_{1N})[|(\psi_1|z\,\psi_{iN})| + \zeta\Sigma_i]^2$$

and

$$f_i^l = \begin{cases} (T_{iN} - E_{1N})[|(\psi_1|z\,\psi_{iN})| - \zeta\Sigma_i]^2 \\ 0 \quad \text{if} \quad |(\psi_1|z\,\psi_{iN})| \le \zeta\Sigma_i \ . \end{cases} \tag{17}$$

III. RESULTS

In Tables I–IV we report samples results for $m = 0$ even-parity states, relative to four situations character-

TABLE II. Columns 1, 3, and 5 and the γ value are the same as in Table I; column 4 is the same as in Table I, but in units of 10^{-4} Ry; column 2: Δ^u values [estimate (19)]. All the energy lower bounds are Temple's. $N = 1540$, and $I = -104.90$ to -95.27 cm^{-1}.

i	Δ (Ry)	σ	$-E_i^u$	f_i^u
241	1.3×10^{-17}	3.9×10^{-12} (3)	9.559 222 020 050 969 738 024 97	0.734 243 905 360 07 89631188
242	1.4×10^{-17}	3.4×10^{-12} (2)	9.525 206 844 746 397 390 986 18	0.202 241 338 600 16 447548
243	1.0×10^{-17}	2.9×10^{-12} (3)	9.473 794 895 371 959 936 114 45	2.085 385 996 805 1 856392
244	8.4×10^{-19}	5.6×10^{-13} (3)	9.439 311 332 600 689 994 567 47	3.524 327 677 499 8 46857
245	1.4×10^{-17}	3.2×10^{-12} (2)	9.424 359 256 813 203 175 690 04	0.743 053 669 167 82 169654
246	1.0×10^{-17}	4.0×10^{-12} (3)	9.301 377 084 728 188 047 530 81	1.525 505 682 550 4 691599
247	1.4×10^{-17}	9.9×10^{-12} (3)	9.275 687 835 735 271 209 166 82	0.028 965 023 448 211 18922439
248	1.4×10^{-17}	3.6×10^{-12} (2)	9.261 101 106 278 498 796 296 64	0.648 354 092 933 37 8531894
249	1.4×10^{-17}	1.8×10^{-12} (3)	9.148 492 706 046 564 840 936 19	1.093 130 131 820 0 267028
250	1.2×10^{-17}	5.1×10^{-11} (3)	9.073 574 836 813 626 875 958 61	2.668 158 500 346 9 2781122
251	1.5×10^{-17}	1.3×10^{-11} (2)	9.071 169 794 035 939 426 524 47	0.488 079 718 727 67 69462839
252	1.4×10^{-17}	7.2×10^{-12} (3)	9.018 261 554 800 413 933 937 41	0.765 856 317 993 24 0108912
253	1.6×10^{-17}	3.9×10^{-12} (2)	8.999 227 922 958 289 412 013 18	0.039 252 110 432 466 08360794
254	1.3×10^{-17}	3.3×10^{-12} (3)	8.907 153 356 962 977 316 878 29	0.596 790 327 671 06 083145
255	1.4×10^{-17}	9.8×10^{-12} (3)	8.868 823 247 469 261 413 160 95	1.954 244 986 542 0 499023
256	1.3×10^{-17}	4.3×10^{-12} (2)	8.854 606 858 944 648 741 445 84	0.301 029 736 912 54 065801
257	1.4×10^{-17}	1.7×10^{-12} (2)	8.785 993 402 045 736 984 528 92	0.616 082 434 799 91 114397
258	1.3×10^{-17}	1.1×10^{-11} (3)	8.694 743 216 386 771 826 574 37	0.528 541 892 092 58 7135851
259	1.5×10^{-17}	6.4×10^{-12} (2)	8.682 319 213 806 630 548 174 34	1.397 387 610 899 9 5906759

ized by a different behavior [2] of the corresponding classical system: regular motion (Table I), the appearance of the first irregular orbits (Table II), the presence of a very high fraction of irregular orbits (Table III), and the absence of regular orbits (Table IV). Our calculations in Tables I–III reproduce, as we said, results which can be found in paper [2]. As one can see, the efficiency of our method decreases as the percentage of the irregular

TABLE III. Columns 1 and 3 as in Table I; columns 2 and 4 as in Table II; column 5 same as in Table I, but in units of 10^{-6}. All the energy lower bounds are Temple's. $N = 5050$, $\gamma = 2.535\times10^{-5}$, $I = -26.96$ to -24.05 cm^{-1}.

i	Δ (Ry)	σ	$-E_i^u$	f_i^u
515	2.6×10^{-13}	2.0×10^{-7} (2)	2.470 609 889 480 5	2.197 641 369 5151327
516	2.3×10^{-13}	9.2×10^{-7} (3)	2.448 513 428 050 5	1.896 124 321 85470384
517	1.5×10^{-13}	1.5×10^{-7} (2)	2.445 963 970 014 0	0.451 084 4711 02068981
518	2.4×10^{-13}	1.8×10^{-7} (3)	2.408 356 658 285 4	2.507 433 003 4982635
519	1.2×10^{-13}	2.0×10^{-7} (3)	2.395 453 269 804 3	5.442 150 117 38195351
520	8.0×10^{-13}	1.2×10^{-6} (2)	2.389 213 071 844 1 5	2.176 467 810 61726290
521	3.1×10^{-13}	3.3×10^{-7} (2)	2.381 840 844 896 2	1.843 552 121 39802881
522	4.3×10^{-13}	3.1×10^{-7} (2)	2.369 282 182 665 8	0.116 800 1253 58912785
523	6.4×10^{-13}	1.4×10^{-6} (3)	2.354 076 587 899 7	0.666 636 4869 568584817
524	3.3×10^{-13}	3.1×10^{-7} (2)	2.349 564 797 472 3	12.028 103 57 1885271
525	7.6×10^{-13}	7.7×10^{-7} (3)	2.325 189 646 244 4	1.711 773 575 03203770
526	7.4×10^{-13}	5.9×10^{-7} (2)	2.315 333 968 031 9	0.608 208 9130 43365664
527	2.5×10^{-12}	1.5×10^{-5} (3)	2.299 260 940 156 2 6	4.965 075 526 688746522
528	2.8×10^{-13}	5.4×10^{-7} (2)	2.297 597 566 033 5	2.856 032 696 48263053
529	1.4×10^{-12}	8.1×10^{-7} (2)	2.282 376 350 441 8 9	0.038 827 39626 748632647
530	9.8×10^{-13}	5.1×10^{-7} (2)	2.263 970 944 160 5	0.035 314 67500 451096480
531	3.3×10^{-12}	5.3×10^{-6} (3)	2.243 501 881 617 1 3	0.094 481 91551 8127475424
532	2.3×10^{-12}	2.4×10^{-6} (2)	2.237 275 022 663 8 9	0.939 736 8140 197250375
533	2.1×10^{-12}	4.2×10^{-6} (3)	2.222 600 294 170 0	3.817 714 743 748380018
534	3.5×10^{-12}	6.5×10^{-6} (2)	2.217 711 600 494 1 3	0.619 265 2825 5764988748
535	5.7×10^{-12}	6.7×10^{-6} (2)	2.211 776 218 550 4 6	4.938 203 943 811872136

motion grows or, equivalently, as the diamagnetic interaction begins to dominate over the Coulomb one. The explanation of this fact was given in Ref. [6]; here we note only that increasing gradually the basis size, one can make up for this behavior of our method. Thus the conjecture in [6] that our method might be applied beyond the regime where the Coulomb interaction is predominant (weak-field regime) is found here to be correct. Another conjecture in [6] is that the parabolic Sturmian basis is probably the most convenient for dealing with Rydberg states in fields of a few tesla. Comparing the basis sizes in the present paper with those in Refs. [1,3] and taking the accuracy of our results into account, one finds that this latter conjecture is also correct. Regarding the results in Tables I–III (range of the energy $-190\ \mathrm{cm}^{-1}$ to $-24\ \mathrm{cm}^{-1}$), our method, although with decreasing accuracy, works at its best. That is to say, the RR method appears to be convergent [11], conditions (7) and (9) are always satisfied, either $E_{iN} \leq \eta_{iN}$ or $E_{iN} \geq \eta_{iN}+\delta_{iN}$ [see formulas (13) and (14)], and finally $|(\psi_1|z\,\psi_{iN})| > \zeta\Sigma_i$ [see Eq. (17)]. As a consequence, we can always give in this case the most accurate error estimates (Temple's lower bounds to energy, either estimate $\sigma_{i(2)}$ or $\sigma_{i(3)}$ for the eigenfunction error, and a lower bound $f_i^l > 0$ for the oscillator-strength value). It should be observed that, strictly speaking, the fulfillment of conditions (7) needs the knowledge of the exact eigenvalues. However, by the convergence of the RR method, here it is enough to replace in (7) E_{i-1}, E_i, E_{i+1} with $E_{i-1,N}, E_{iN}, E_{i+1,N}$. Table IV shows that, even working with a large basis ($N = 5050$), our method presents some difficulty above $\sim -24\ \mathrm{cm}^{-1}$. The upper bounds on the eigenvalues in Table IV can be still considered of good reliability, but, in some cases, the lower bounds are only the less accurate Weinstein bounds. These are rigorous (in the sense that the interval $(W_{iN}, E_{iN}]$ contains the only eigenvalue E_i) if conditions (7) are satisfied; otherwise, as shown in Ref. [6], it may happen that W_{iN} is a lower bound to E_k ($k < i$) as well. In any case, as we said in Sec. II, in the presence of Weinstein's lower bounds, no eigenfunction-error estimates (and consequently no oscillator strength error estimates) can be given. According to the calculations of the present paper, however, it seems reasonable to expect that our method might also be successful over the energy range of Table IV or even at higher energies, if one works with sufficiently large bases on a supercomputer. With reference to this point, it should be observed that, in order to save memory and computing time of

TABLE IV. Columns 1 and 3 are the same as in Table I; columns 2 and 4 are the same as in Table II; blank space in column 3 means that either $\sigma_{i(1)}$ or $\sigma_{i(2)} = 1$ or that formula (14) cannot be applied. All the energy lower bounds are Temple's, except those marked by (W) [Weinstein's lower bounds, formula (8)]. Column 5 (f) reports (in units of 10^{-7}) only the approximate values of the oscillator strengths, i.e., $(E_{iN} - E_{1N})(\psi_{1N}|z\psi_{iN})^2$, because in this case the error interval $[f_i^l, f_i^u]$ turns out to be too large. N and γ are the same as in Table III, $I = -16.93$ to -12.51 cm^{-1}.

i	Δ (Ry)	σ	$-E_l^u$	f
600	8.5×10^{-8}	1.6×10^{-1} (2)	1.543 054 084 134524	4.311 970 288
605	1.1×10^{-7}	1.1×10^{-1} (2)	1.500 172 786 270879	0.421 075 2139
610	1.4×10^{-7}	2.4×10^{-1} (2)	1.451 781 272 992061	9.248 899 340
615	1.8×10^{-7}	3.3×10^{-1} (3)	1.404 444 666 5072361	49.249 849 13
620	1.9×10^{-7}	2.6×10^{-1} (2)	1.370 049 400 458945	1.677 731 946
625	2.6×10^{-7}		1.327 870 367 30467884 (W)	4.669 441 570
630	3.0×10^{-7}		1.291 976 700 4976781 (W)	0.336 642 4699
635	3.3×10^{-7}	6.8×10^{-1} (1)	1.252 587 571 5606070	4.452 179 956
640	4.4×10^{-7}		1.213 791 349 8183136 (W)	8.099 233 736
645	8.6×10^{-7}		1.176 071 569 84710289 (W)	3.248 659 940
650	4.6×10^{-6}		1.139 834 112 85693231 (W)	0.100 415 9659

the computer used by us (Dec Alpha 3000/500), the calculation of the quantity Δ_{iN} [see Eq. (4)], in the cases $N = 1540$ and $N = 5050$, has been performed using only a part of the matrix corresponding to the operator B^{-1} and then evaluating the error coming from this truncation. In order to illustrate this point, we note first that the quantity Δ_{iN} can be written [6] as

$$\Delta_{iN} = \langle \chi_{iM} | B^{-1} \chi_{iM} \rangle^{1/2},$$

where $\chi_{iM} = (A - E_{iN}B)\psi_{iN}$ is an M-component vector ($M > N$). Introducing now the orthogonal projection operators [according to the topology of $L^2(\mathbb{R}^{++}, du\,dv)$] P_N and P_{M-N}, where P_N projects on the subspace spanned by the basis vectors $\phi_1, \phi_2, \ldots, \phi_N$ and P_{M-N} projects on the subspace spanned by the basis vectors $\phi_{N+1}, \phi_{N+2}, \ldots, \phi_M$, one can write

$$\begin{aligned}\Delta_{iN}^2 = {} & \langle P_N \chi_{iM} | B_N^{-1} P_N \chi_{iM} \rangle \\ & + 2 \langle P_N \chi_{iM} | B_{N,M-N}^{-1} P_{M-N} \chi_{iM} \rangle \\ & + \langle P_{M-N} \chi_{iM} | B_{M-N}^{-1} P_{M-N} \chi_{iM} \rangle . \end{aligned} \tag{18}$$

Since $P_N \chi_{iM} = (A_N - E_{iN} B_N)\psi_{iN}$ [RR truncation of Eq. (2)] is of order 10^{-15}, the main contribution to the value of Δ_{iN} comes from the last term in Eq. (18). Denoting by $\widetilde{\Delta}_{iN}^2$ its value, we have

$$\begin{aligned} |\Delta_{iN}^2 - \widetilde{\Delta}_{iN}^2| = {} & |\langle P_N \chi_{iM} | B_N^{-1} P_N \chi_{iM} \rangle \\ & + 2 \langle P_N \chi_{iM} | B_{N,M-N}^{-1} P_{M-N} \chi_{iM} \rangle| \\ \le {} & |P_N \chi_{iM}|^2 \, |B_N^{-1}| \\ & + 2 |P_N \chi_{iM}| \, |P_{M-N} \chi_{iM}| \, |B_{N,M-N}^{-1}| \le \alpha, \end{aligned}$$

where α is obtained by computing the vector norms $|P_N \chi_{iM}|$ and $|P_{M-N}\chi_{iM}|$ and estimating the matrix norms $|B_N^{-1}|$ and $|B_{N,M-N}^{-1}|$. Thus we can write

$$\Delta^l \equiv \sqrt{\widetilde{\Delta}_{iN}^2 - \alpha} \le \Delta_{iN} \le \sqrt{\widetilde{\Delta}_{iN}^2 + \alpha} \equiv \Delta^u. \tag{19}$$

The quantity $\Delta^u - \Delta^l$ varies from about 10^{-17} (Table II) to about 10^{-13} (Table IV). The results in Tables II–IV have been obtained taking for Δ_{iN} the most unfavorable estimate, i.e., $\Delta_{iN} = \Delta^u$.

IV. CONCLUSION

In conclusion, with the present paper we have extended our previous work [5,6], improving the accuracy of results, showing the efficiency of the method up to highly excited Rydberg states, and determining upper and lower bounds to oscillator strengths. Our results (at least in the energy range of -190 cm^{-1} to -24 cm^{-1}) are also much more accurate than those in the literature. Indeed, in this energy range our energy values have an accuracy varying from 13 to 24 significant digits and the oscillator strengths (except some cases in Table III) have an accuracy of two to ten significant digits. On the contrary, in Refs. [1–3] one has an accuracy of six to seven significant digits for the energy and of two to three significant digits for the oscillator strengths. It should be observed that in the case of Tables I and II, we have actually obtained energy eigenvalues with an accuracy even higher than that mentioned above, i.e., up to 29 significant digits. Of course, such levels of accuracy are only of academic interest. However, for the Rydberg states considered here, an accuracy of at least 10–12 significant digits for the nonrelativistic energy is expected to be [6] a necessary requirement to evaluate secondary contributions to the binding energy, such as those due to the relativistic effects, to the QED corrections, to the nuclear structure, etc. Given the high accuracy of the oscillator-strength values in Tables I and II, we have also been able to estimate, in this case, the effect of approximating the state ψ_1 in (15) with the corresponding unperturbed hydrogenic eigenfunction. We have thus found that this approximation gives rise to an error of some parts in 10^9 to some parts in 10^7. Finally, we want to stress that the accuracy of our results is on a rigorous footing, in the sense that it has been obtained by means of an upper-lower bound technique. On the contrary, in the literature, the accuracy of results is usually estimated numerically, i.e., by varying the size of the basis employed and the corresponding nonlinear variational parameter.

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[10] In correspondence with the two values of γ employed in the present paper ($\gamma = 2.55 \times 10^{-5}$ and $\gamma = 2.535 \times 10^{-5}$) we have found, respectively, $\zeta = 4.242\,640\,657\,692\,3$ and $\zeta = 4.242\,640\,658\,037\,5$.

[11] The convergence of the RR method in the present paper has been verified numerically. The question of the analytical convergence of our RR method has been discussed in Ref. [6].