PHYSICAL REVIEW A VOLUME 54, NUMBER 2 AUGUST 1996

Direct calculation of Stark resonances in hydrogen

Francisco M. Fernández
CEQUINOR, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 115, Casilla de Correo 962,
1900 La Plata, Argentina

(Received 28 September 1995)

We propose an alternative way of calculating the resonances of the Stark effect in hydrogen. The method is based on a rational approximation of the logarithmic derivative of the eigenfunction, and leads to a quantization condition for the complex energies of the metastable states. We present accurate results for the ground and some excited states for several field intensities. [S1050-2947(96)07007-2]

PACS number(s): 32.60.+i, 03.65.Ge

I. INTRODUCTION

The dc Stark effect in hydrogen is an old problem in quantum mechanics. Because of the external electric field, the Hamiltonian operator is unbounded and the discrete spectrum of the isolated hydrogen atom is completely destroyed. However, there are metastable or resonance states embedded in the continuum characterized by complex energy eigenvalues. Their real and imaginary parts determine the positions and widths of the resonances, respectively. The real part of any such eigenvalue is interpreted as the energy of a metastable state with a lifetime related to the inverse of the corresponding imaginary part.

The Rayleigh-Schrödinger perturbation series is known to be divergent but asymptotic to the resonance position. However, one can still obtain the resonance position and width by means of Borel-Padé approximants [1], Hermite-Padé approximants [2], or analytic continuation of the perturbation series into the complex plane [3,4]. Alternative perturbation approaches applied to the Stark effect in hydrogen are the $1/n$ expansion [2] based on a WKB method [5] and the summation of a large-D expansion by means of Hermite-Padé approximants [6]. Here n is the principal quantum number of hydrogen, and D is the spatial dimension.

Among the nonperturbative approaches we mention complex scaling (or complex coordinate rotation) [5–10], numerical integration of the second-order differential equations [11,12], power series expansions [13], an expansion in a basis set of harmonic-oscillator eigenfunctions [14], minimization of the variance [15,16], and Weyl's theory [17].

There is a vast literature on the Stark effect in hydrogen; here we only mention articles related in some way or another to the present one. The reader may find additional references in those already quoted, and particularly in a short review of the mathematical and computational aspects of the atomic dc Stark effect in an appendix in one of them [9].

In this paper we obtain the Stark resonances for hydrogen by means of the Riccati-Padé method, which has been demonstrated to be useful for the calculation of bound-state eigenvalues [18–23] and resonances [24,25] for simpler models. In Sec. II we show how to apply the Riccati-Padé method to the Stark effect in hydrogen, and in Sec. III we present and discuss results for the ground and some excited states.

II. RICCATI-PADÉ METHOD FOR THE STARK EFFECT IN HYDROGEN

In atomic units the Schrödinger equation for a hydrogen atom in a dc electronic field of intensity F reads

$$\left(\nabla^2+\frac{2}{r}-2Fz+2E\right)\Psi(x,y,z)=0. \tag{1}$$

It is separable in parabolic or squared parabolic coordinates [17]. Here we arbitrarily choose the former given by $x=\sqrt{\xi\eta}\cos\phi$, $y=\sqrt{\xi\eta}\sin\phi$, and $z=(\xi-\eta)/2$, where $\xi\geqslant 0$, $\eta\geqslant 0$, and $0\leqslant\phi<2\pi$. Writing the solution to (1) as $\Psi(x,y,z)=(\xi\eta)^{-1/2}u(\xi)v(\eta)e^{im\phi}$, $m=0,\pm1,\pm2,\ldots$, we obtain

$$\left(\xi\frac{d^2}{d\xi^2}+\frac{1-m^2}{4\xi}+\frac{E}{2}\xi-\frac{F}{4}\xi^2+A_1\right)u(\xi)=0, \tag{2a}$$

$$\left(\eta\frac{d^2}{d\eta^2}+\frac{1-m^2}{4\eta}+\frac{E}{2}\eta+\frac{F}{4}\eta^2+A_2\right)v(\eta)=0, \tag{2b}$$

where A_1 and $A_2=1-A_1$ are separation constants. These equations are of the form

$$\left(x\frac{d^2}{dx^2}+\frac{1-m^2}{4x}+\frac{E}{2}x-\sigma\frac{F}{4}x^2+A\right)\Phi(x)=0, \tag{3}$$

where A stands for either A_1 or A_2 when $\sigma=1$ or $\sigma=-1$, respectively.

In the Riccati-Padé method we consider the regularized logarithmic derivative of the eigenfunction

$$f(x)=\frac{s}{x}-\frac{\Phi'(x)}{\Phi(x)}, \tag{4}$$

where s is chosen to be $(|m|+1)/2$ in order to remove the pole of $\Phi'(x)/\Phi(x)$ at $x=0$. The function $f(x)$ is a solution of the Riccati equation

$$xf'+2sf-xf^2-\frac{E}{2}x+\sigma\frac{F}{4}x^2-A=0. \tag{5}$$

Since $f(x)$ is analytic at $x=0$ we can expand it in a Taylor series about that point,

TABLE I. Convergence of the Riccati-Padé method for the ground state when $F=0.1$.

D	E A	
2	-0.530	
	0.555	
3	-0.5273	$-0.0071i$
	$0.533\,87$	$+0.0030i$
4	$-0.527\,413$	$-0.007\,269\,5i$
	$0.553\,913$	$+0.003\,089\,5i$
5	$-0.527\,418\,13$	$-0.007\,269\,2i$
	$0.553\,914\,96$	$+0.003\,089\,32i$
6	$-0.527\,418\,176$	$-0.007\,269\,059i$
	$0.553\,914\,983$	$+0.003\,089\,283\,2i$
7	$-0.527\,418\,175\,1$	$-0.007\,269\,056\,78i$
	$0.553\,914\,983\,0$	$+0.003\,089\,282\,48i$
E [14]	$-0.527\,418\,175\,09$	$-0.007\,269\,056\,76i$

$$f(x)=\sum_{j=0}^{\infty} f_j(E,A,F)x^j. \tag{6}$$

One readily obtains the coefficients f_j from the recurrence relation

$$f_n=\frac{1}{n+2s}\left(\sum_{j=0}^{n-1} f_j f_{n-j-1}+A\delta_{n0}+\frac{E}{2}\delta_{n1}-\sigma\frac{F}{4}\delta_{n2}\right), \tag{7}$$

which follows from the Riccati equation (5).

Except for the ground state, the function $f(x)$ will have simple poles at the zeros of $\Phi(x)$ for $x>0$. Therefore, a rational function seems to be a natural representation of $f(x)$. In the Riccati-Padé approach we require that the Padé approximant satisfies

$$\frac{\sum_{j=0}^{N+d} a_j x^j}{\sum_{j=0}^{N} b_j x^j}=\sum_{j=0}^{2N+d+1} f_j x^j, \quad N=1,2\ldots,d=0,1,\ldots. \tag{8}$$

The system of equations for the coefficients b_j exhibits nontrivial solutions provided that E and A satisfy the quantization condition [18–25]

$$H_D^d(E,A,F)=\begin{vmatrix} f_{d+1} & f_{d+2} & \cdots & f_{D+d} \\ f_{d+2} & f_{d+3} & \cdots & f_{D+d+1} \\ & & \ddots & \\ f_{D+d} & f_{D+d+1} & \cdots & f_{2D+d-1}\end{vmatrix}=0, \tag{9}$$

TABLE II. Values of E and A for the ground state.

F		
0.03	$E=-0.502\,074\,272\,61$	$-1.118\,6\times10^{-8}i$
	$A=0.484\,905\,008\,06$	$+5.294\times10^{-9}i$
	$E=-0.502\,074\,272\,60$	$-1.118\,80\times10^{-8}i$ [14]
0.5	$E=-0.623\,068\,025\,6$	$-0.279\,744\,825\,0i$
	$A=0.693\,937\,489\,58$	$+0.089\,015\,929\,1i$
1	$E=-0.624\,336\,507\,1$	$-0.646\,820\,899\,5i$
	$A=0.786\,338\,516\,4$	$+0.176\,295\,975\,9i$
	$E=-0.624\,336\,507\,36$	$-0.646\,820\,900\,08i$ [14]
10	$E=0.608\,271\,705\,6$	$-5.578\,015\,929$
	$A=1.324\,400\,164\,7$	$+0.833\,391\,481i$
	$E=0.608\,271\,705\,47$	$-5.578\,015\,928\,2i$ [14]

where $D=N+1$ is the dimension of the matrix.

Equation (3) is invariant under the substitution of $-x$, $-A$, and $-F$ for x, A, and F, respectively. For this reason, if (9) is the Hankel determinant for (2a) ($\sigma=1$, $A_1=A$), then $H_D^d(E,A-1,F)$ is the Hankel determinant for (2b) ($\sigma=-1$, $A_2=1-A$), and the pair of equations

$$H_D^d(E,A,F)=0, H_D^d(E,A-1,F)=0 \tag{10}$$

completely determine E and A. The main assumption of the Riccati-Padé method is that the common roots of the Hankel determinants (10) converge toward the physical values of E and A coming from (2a) and (2b), for a given value of F, as D increases.

Although, to our knowledge, no general rigorous proof of the convergence of the Riccati-Padé method has ever been given, there are reasons to believe the assumption above to be true, at least in some cases. First, the Riccati-Padé method gives exact results for solvable models such as the harmonic oscillator, the hydrogen atom, etc. [19]. Second, it has been proved that the method yields upper and lower bounds for some nontrivial examples [19]. Third, the quantization condition (9) appears to be compatible with the physical asymptotic behavior of $f(x)$ [22,23]. Fourth, the method yields the exact weak-coupling expansion (Rayleigh-Schrödinger perturbation series) for some simple quantum-mechanical models [22].

Here we verify numerically that the quantization condition given by (9) and (10) applies to the Stark effect in hydrogen. Notice that the present approach does not take into account the asymptotic form of the eigenfunction explicitly. In fact, one treats bound states and resonances in the same way. The Riccati-Padé method shares this appealing feature with other approaches such as, for example, the complex scaling method [7–10] and the minimization of the variance [15,16].

III. RESULTS AND DISCUSSION

For a given value of the field intensity F, the coefficients f_j, and, consequently, the Hankel determinants H_D^d, are polynomial functions of E and A. In the Riccati-Padé method the problem of obtaining the Stark resonances reduces to the calculation of common roots of the two polyno-

TABLE III. Values of E and A for two resonance states with $m>0$.

	$m=1$	
F		
0.004	$E=-0.126 316 885 21$	$-4.05\times 10^{-7}i$
	$A=0.475 642 877 45$	$-7.44\times 10^{-7}i$
	$E=-0.126 316 885$	$-4.05\times 10^{-7}i$ [12]
0.008	$E=-0.131 261 459 9$	$-0.001 036 240 5i$
	$A=0.551 629 821 5$	$+0.001 769 937 7i$
	$E=-0.131 188 59$	$-0.001 012 2i$ [12]
0.012	$E=-0.137 578 109 2$	$-0.006 098 481 7i$
	$A=0.578 268 435 1$	$+0.009 792 030 8i$
	$E=-0.135 971 6$	$-0.005 843 5i$ [12]
0.016	$E=-0.142 721 569 4$	$-0.013 474 643 5i$
	$A=0.600 925 393 1$	$+0.020 590 590 3i$
	$E=-0.136 437$	$-0.013 776i$ [12]
0.02	$E=-0.146 729 380 6$	$-0.021 853 640 4i$
	$A=0.620 417 948 9$	$+0.032 056 127 7i$
	$E=-0.131 50$	$-0.025 940 5i$ [12]
	$m=9$	
F		
0.0001	$E=-0.006 425 985 2$	$-0.003 369 409 7i$
	$A=0.712 889 313 00$	$+0.103 509 316 8i$
	$E=-0.006 425 5$	$-0.003 369 5i$ [2]
	$E=-0.006 426$	$-0.003 369 4i$ [2]

mials (10). Here we apply the Newton-Raphson algorithm for increasing values of D, and examine the convergence of the method.

For sufficiently small field intensities the resonance positions are close to the energies of the isolated hydrogen atom, and the widths are exponentially small [26]. In such cases the Riccati-Padé method, which gives exact results at $F=0$, yields the resonances positions with great accuracy even with determinants of small dimension. Conversely, to obtain the corresponding widths one has to resort to large determinants. If, on the other hand, F is not too small, then Hankel determinants of moderate dimension yield both positions and widths with acceptable accuracy. This feature makes the Riccati-Padé method complementary to the semiclassical approximations, which produce accurate lifetimes when there is little electron leakage through the potential barrier.

For simplicity we concentrate on those resonance states with functions $u(\xi)$ and $v(\eta)$ which do not have zeros for $\xi,\eta>0$. The greater the number of such nodes, the greater the dimension of the Hankel determinants required for a given accuracy. Here we restrict ourselves $D\leqslant 7$ and arbitrarily choose $d=0$ (values of $d>0$ yield results of comparable accuracy). Table I shows that the roots of the Hankel determinants for $F=0.1$ converge rapidly toward the complex eigenvalues calculated by other accurate methods, such as, for example, the expansion in a basis set of harmonic-oscillator eigenfunctions [14]. The converged results for the ground state at some other values of F given in Table II also agree with the calculation based on an expansion in a basis set of harmonic-oscillator eigenfunctions, which appears to be the most accurate method applied to this problem [14].

In Table III we show results for excited states with $m=1$ and 9. In the former case our results agree with those obtained by numerical integration and power-series representation only for small field strengths [12]. Our result for $m=9$ is found to be in agreement with the result obtained using the summation of the perturbation series by Hermite-Padé approximants and also with the result obtained by the $1/n$ expansion [2].

Present numerical investigation suggests that the Riccati-Padé method converges rapidly toward the resonances of the Stark effect in hydrogen for all values of the field strength. The simplicity of the theory, and the fact that the asymptotic form of the eigenfunction does not appear explicitly in the calculation, are two appealing features of the approach. With respect to the latter, it is worth stressing that the same quantization condition applies to bound states and resonances. It appears as if the Riccati-Padé method provided the poles of the scattering matrix [27]. We are presently investigating this fact by means of simple mathematical models [28].

A disadvantage of the Riccati-Padé method is that it may not be practical for highly excited states with strongly oscillating eigenfunctions. Such states require Padé approximants with denominators of large order and, consequently, Hankel determinants of great dimension. Another limitation of the present form of the Riccati-Padé method is that it only applies to separable problems. We expect to develop a modified approach free from such a deficiency.

ACKNOWLEDGMENTS

We thank the Quantum Theory Project at the University of Florida for computational facilities.

[1] V. Franceschini, V. Grechi, and H. J. Silverstone, Phys. Rev. A **32**, 1338 (1985).
[2] V. S. Popov, V. D. Mur, A. V. Sergeev, and V. M. Weinberg, Phys. Lett. A **149**, 418 (1990).
[3] J. N. Silverman and C. A. Nicolaides, Chem. Phys. Lett. **153**, 61 (1988).
[4] B. G. Adams, *Algebraic Approach to Simple Quantum Systems. With Applications to Perturbation Theory* (Springer-Verlag, Berlin, 1994), p. 158.
[5] J. D. Bekenstein and J. B. Krieger, Phys. Rev. **188**, 130 (1969).
[6] T. Germann and S. Kais, J. Chem. Phys. **99**, 7739 (1993).
[7] W. P. Reinhardt, Int. J. Quantum Chem. Symp. **10**, 359 (1976).
[8] E. Brändas and P. Froelich, Phys. Rev. A **16**, 2207 (1977).
[9] C. Cerjan, R. Hedges, C. Holt, W. P. Reinhardt, K. Scheibner,

and J. J. Wendoloski, Int. J. Quantum Chem. **14**, 393 (1978).

[10] A. Maquet, S.-I. Chu, and W. P. Reinhardt, Phys. Rev. A **27**, 2946 (1983).

[11] J. O. Hirschfelder and L. A. Curtis, J. Chem. Phys. **55**, 1395 (1971).

[12] R. J. Damburg and V. V. Kolosov, J. Phys. B **9**, 3149 (1976).

[13] M. H. Alexander, Phys. Rev. **178**, 34 (1969).

[14] L. Benassi and V. Grecchi, J. Phys. B **13**, 911 (1980).

[15] P. Froelich and E. Brändas, Phys. Rev. A **12**, 1 (1975).

[16] P. Froelich and E. Brändas, Int. J. Quantum Chem. Symp. **10**, 353 (1976).

[17] M. Hehenberger, H. V. McIntosh, and E. Brändas, Phys. Rev. A **10**, 1494 (1974).

[18] F. M. Fernández, Q. Ma, and R. H. Tipping, Phys. Rev. A **39**, 1605 (1989).

[19] F. M. Fernández, Q. Ma, and R. H. Tipping, Phys. Rev. A **40**, 6149 (1989).

[20] F. M. Fernández, Q. Ma, D. J. DeSmet, and R. H. Tipping, Can. J. Phys. **67**, 931 (1989).

[21] F. M. Fernández, Phys. Lett. A **166**, 173 (1992).

[22] F. M. Fernández and R. Guardiola, J. Phys. A **26**, 7169 (1993).

[23] F. M. Fernández, R. Guardiola, and M. Znojil, Phys. Rev. A **48**, 4170 (1993).

[24] F. M. Fernández, J. Phys. A **28**, 4043 (1995).

[25] F. M. Fernández, Phys. Lett. A **203**, 275 (1995).

[26] M. H. Rice and R. H. Good Jr., J. Opt. Soc. Am. **52**, 239 (1962).

[27] A. Martin, Nuovo Cimento **14**, 403 (1959).

[28] F. M. Fernández, J. Phys. A (to be published).