

Different Approach to the Stark Effect: Application to the Excited States of Hydrogen Atom

O. L. Silva Filho, A. L. A. Fonseca, H. N. Nazareno and P. H. A. Guimarães

Departamento de Física, Universidade de Brasília, 70910-900, Brasília, DF, Brasil

Received March 3, 1992; revised manuscript received July 28, 1992

The application of a semi-analytical method introduced by the present authors in a previous work has enabled us to calculate the excited energy levels and wave functions associated with the Stark effect on a Hydrogen atom. The method is a variational one and we used algebraic computation to solve it. We present the results to the $n = 2$ and $n = 3$ levels. It is shown that in these cases the method works as well as it does for the ground state. On the other hand the wave functions associated with the stationary states show the probability of autoionization by tunneling in the limit of high fields.

I. Introduction

The study of the Stark effect for strong fields was the subject of great interest, mainly for the excited states, due to the existence of experimental data on Rydberg states. Among the different theoretical approaches found in the literature, we quote the following: perturbation methods¹⁻³, $1/n$ expansion^{4,5}, WKB calculations^{6,7}, numerical⁸⁻¹² and complex scaling¹³ methods, scattering phase studies¹⁴ and expansion in Sturmian functions¹⁵.

In a previous paper¹⁶ we have presented a semi-analytical method through which one can calculate the eigenfunctions and eigenvalues of the Hydrogen atom under a uniform static electric field. As an application we have solved the corresponding Schrödinger equation for the ground state. To apply the method to the excited states we have modified slightly the wave function with respect to that adopted in our previous work in order to improve our results.

The proposed method is posed in variational form¹⁷ and the determination of the coefficients that appear in the trial function is obtained via an algebraic computation procedure; that is why we have called it semi-analytical. In brief, the method¹⁶ consists in solving the Schrödinger equation in parabolic-cylindrical coordinates and expanding the wavefunction in terms of Laguerre functions plus polynomials in a way that for the field-free case the expansion reduces to the exact wavefunction for the Hydrogen atom. This procedure leads to a transcendental equation for the energy eigenvalues which is solved through a self-consistent procedure. Even for the excited states the expansion for the wave function includes only a few terms, which shows the rapid convergence of our method.

In section II we present the method of calculus, while in section III we show the results obtained for the two first excited levels $n = 2$ and $n = 3$. Finally in

section IV we present a discussion of these results

II. The Method

For the treatment of the excited states we propose a wave function of the form

$$\psi(u, v, \phi) = N(uv)^{|m|/2} e^{-(u+v)/2} e^{-m\phi} [a_0 L_{n_1}^{|m|}(u) + Q_1(u)][b_0 L_{n_2}^{|m|}(v) + Q_2(v)] \quad (1)$$

where N is a normalization constant, m is the magnetic quantum number, a_0 and b_0 are constants, $L_n^m(x)$ is the Laguerre function, the dimensionless coordinates u and v are defined by

$$u = \gamma(r+z)/2 \quad ; \quad v = \gamma(r-z)/2, \quad (2)$$

the energy parameter is defined by

$$\gamma = (-2E)^{1/2}, \quad (3)$$

and $Q_1(u)$ and $Q_2(v)$ are polynomials.

The idea of expressing the wave function in the form of Laguerre function plus a polynomial is to make the connection between the field-free case and the perturbed system wave function. In this way, when the field is zero the wave function automatically gives the correct indices for the corresponding level.

The differential equations that must be satisfied by the polynomials $Q_1(u)$ and $Q_2(v)$ are

$$uQ_1''(u) + [1 + |m|^{-u}]Q_1'(u) + \left[n_1 + f_1(g_1) + g_1 \frac{u^2}{4} \right] Q_1(u) + \left[f_1(g_1) + g_1 \frac{u^2}{4} \right] L_{n_1}^{|m|}(u) = 0 \quad (4)$$

and

$$\begin{aligned}
 &vQ''_2(v) + [1 + |m|^{-v}]Q'_2(v) \\
 &+ \left[n_2 + f_2(g_1) + g_1 \frac{v^2}{4} \right] Q_2(v) \\
 &+ \left[f_2(g_1) + g_1 \frac{v^2}{4} \right] L_{n_2}^{|m|}(v) = 0, \quad (5)
 \end{aligned}$$

where $f_1(g_1)$ and $f_2(g_1)$ are separation constants such that $f_1(0) = f_2(0) = 0$, and n_1 and n_2 are the parabolic quantum numbers defined by the relation

$$n = n_1 + n_2 + |m| + 1, \quad (6)$$

where n is the principal quantum number.

The energy eigenvalues are the solutions of the transcendental equation

$$E = \frac{1}{2[n + f_1(g_1) + f_2(g_1)]^2} \quad (7)$$

Equation (7) makes explicit the dependence of the energy with the separation constants $f_1(g_1)$ and $f_2(g_1)$, where $g_1 = g/\epsilon^{3/2}$ is the normalized field strength as introduced in Ref. 16.

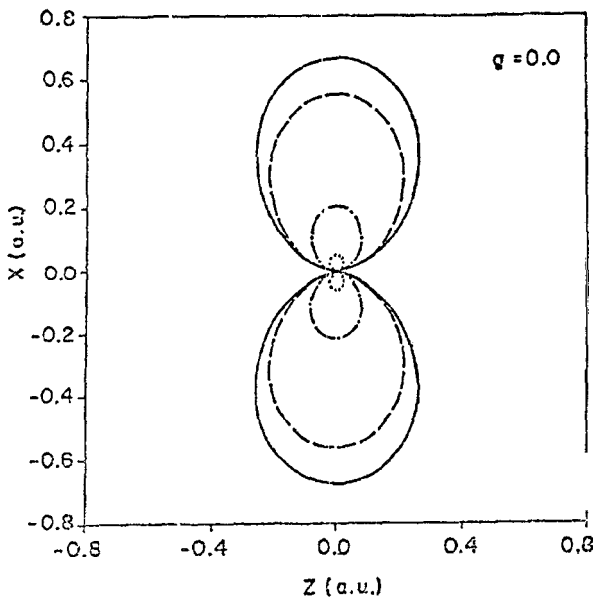


Figure 1: Contour plot of the angular probability density in the relevant x-z plane (not normalized) for the following values of the radial distance r : 2.0 (—), 3.0 (- - - - -), 5.0 (- · - · - ·), and 7.0 (.....). The applied field is $g = 0.0$ a.u. (field free case) and quantum numbers $(2,0,0,+1)$.

Table I.a - Energies in a.u. of Stark effect for the three $n = 2$ levels $(2,1,0,0)$, $(2,0,1,0)$ and $(2,0,0,\pm 1)$, for various values of the field strength.

field (a.u.)	$(2,0,0,1)$ degree 12	$(2,0,1,0)$ degree 19	$(2,1,0,0)$ degree 18
0.00000	-0.125000	-0.125000	-0.125000
0.00100	-0.125078	-0.128086	-0.122083
0.00200	-0.125316	-0.131353	-0.119327
0.00300	-0.125720	-0.134826	-0.116733
0.00400	-0.126308	-0.135447	-0.114305
0.00500	-0.127101	-0.142656	-0.112066
0.00600	-0.128131	-0.147918	-0.110031
0.00700	-0.129442	-	-
0.00800	-0.131081	-	-

Table I.b - Energies of Stark effect for the three $n = 2$ levels $(2,1,0,0)$, $(2,0,1,0)$ and $(2,0,0,\pm 1)$, for field strength 0.005 a.u. (a) Ref. 12, (b) Ref. 15 and (c) present calculation.

level	$(2,0,0,\pm 1)$	$(2,0,1,0)$	$(2,1,0,0)$
(a)	-0.127146	-0.142618	-0.112061
(b)	-0.127146	-0.142618	-0.112061
(c)	-0.127101	-0.142656	-0.112066

Table II - Normalization constant, continuum probability and parabolic turning points for the level $(2,0,0,\pm 1)$, for various values of the field strength.

field (a.u.)	normalization constant	continuum probability	turning points u,v (a.u.)	
0.0000	14.17963081	-	-	-
0.0005	14.18505983	0.130582×10^{-83}	246.00	3.961
0.0010	14.20145624	0.186438×10^{-37}	121.00	3.924
0.0015	14.22917128	0.869841×10^{-22}	79.38	3.888
0.0020	14.26880946	0.135576×10^{-14}	58.56	3.854
0.0025	14.32128819	0.107841×10^{-10}	46.07	3.822
0.0030	14.38784261	0.240367×10^{-08}	37.75	3.791
0.0035	14.47012943	0.758842×10^{-07}	31.80	3.762
0.0040	14.57031645	0.755455×10^{-06}	27.35	3.734
0.0045	14.69126805	0.381336×10^{-05}	23.88	3.707
0.0050	14.83697195	0.135881×10^{-04}	21.11	3.682
0.0055	15.01251947	0.464942×10^{-04}	18.85	3.657
0.0060	15.22564692	0.154578×10^{-03}	16.96	3.634
0.0065	15.48766260	0.465987×10^{-03}	15.36	3.613
0.0070	15.81652273	0.122139×10^{-02}	14.00	3.592
0.0075	16.2362702	0.279421×10^{-02}	12.82	3.572
	16.79809486	0.566693×10^{-02}	11.79	3.554

III. Application of The Method to The First Excited States

We shall treat in detail the application of the method to the first excited levels:

a) The $n = 2$ case:

The first consequence of the action of the electric field is that the spherical symmetry is broken. If we consider the field along the z -axis, the four (one s and three p 's) field-free degenerate levels (not including spin) will split. The degeneracy between p_y and p_x will be preserved, so that three new energy levels will arise when the atom is placed under an electric field: a double degenerate one associated to p_x and p_y states and two single degenerate levels from the s and p_z states.

The equations (4) and (5) for the $n = 2$ case give rise to three pairs of differential equations in u and v , corresponding to the set of quantum numbers $(n, n_1, n_2, |m|)$; i.e. $(2,1,0,0)$, $(2,0,1,0)$ and $(2,0,0,1)$.

In Table I.a we present the energy levels for these three cases as functions of the field strength for expansions of Q_1 and Q_2 that include polynomials of degree 12 until 18: for a energy convergence criterion of the order of 10^{-6} a.u. this will suffice to deal with field strengths up to $g = 0.006$ a.u.. The reliability of our method can be examined in Table I.b, where we have compared our results to those obtained by Kolosov¹⁵

and Telnov¹² for the field intensity of 0.005 a.u. For greater values of the field the expansion can be continued until convergence is obtained. Of course, above some values of the field the probability of autoionization of the electron becomes high and the proposed wave function ceases to be a good choice.

In Table II we calculate the values of the normalization constant and the continuum probability (as defined in Ref. 16), together with the classical turning points in parabolic coordinates, as function of the field strength. Since the continuum probability gives a way to see how near the autoionization the electron is, we can see that the correct trend is reproduced.

In Table III we calculate the average r -values and z -values to study the behavior of the probability density as the field strength is increased. As expected, the electron density is stretched along the positive z -direction and becomes more delocalized as the field strength increases. We also list in Table III the classical turning points for r and z . One can see that for large values of the electric field the electron is pushed away from the nucleus. This fact is associated to the increase in the probability of tunneling to the continuous region.

In Figures 1 and 2 we plot the behaviour of the electronic density in polar coordinates where we have fixed the radial distance and vary the polar angle. This was done for various values of the radial distance and for a value of the field equal to 0.0 a.u. (field free case) and 0.004 a.u., respectively. We note that for small

Table III - Values of r-average and z-average compared with the classical turning point for various values of the field strength.

field (a.u.)	r-average (a.u.)	z-average (a.u.)	turning points r,z (a.u.)	
0.00000	5.00000	0.00000	-	-
0.00025	5.00504	0.03901	499.98	492.02
0.00050	5.00218	0.07811	249.96	242.04
0.00075	5.00492	0.11737	166.60	158.72
0.00100	5.00878	0.15690	124.92	117.07
0.00125	5.01380	0.19677	99.90	92.09
0.00150	5.02001	0.23708	83.21	75.44
0.00175	5.02747	0.27794	71.28	63.55
0.00200	5.03623	0.31945	62.37	54.64
0.00225	5.04637	0.36174	55.37	47.71
0.00250	5.05797	0.40493	49.79	42.17
0.00275	5.07112	0.44916	45.23	37.63
0.00300	5.08595	0.49458	41.42	33.86
0.00325	5.10257	0.54137	38.19	30.67
0.00350	5.12115	0.58972	35.43	27.93
0.00375	5.14115	0.63983	33.02	25.56
0.00400	5.16490	0.69197	30.92	23.49
0.00425	5.19054	0.74642	29.06	21.66
0.00450	5.21910	0.80355	27.41	20.04
0.00475	5.25111	0.86392	25.29	18.59
0.00500	5.28695	0.92797	24.59	17.29
0.00525	5.32743	0.99654	23.38	16.11
0.00550	5.37355	1.07070	22.27	15.03
0.00575	5.42667	1.15185	21.27	14.06
0.00600	5.48861	1.24188	20.34	13.16
0.00625	5.56187	1.34336	19.49	12.34
0.00650	5.64964	1.45961	18.69	11.58
0.00675	5.75618	1.59495	17.97	10.88
0.00700	5.88684	1.75489	17.29	10.23
0.00725	6.04831	1.94625	16.65	09.62
0.00750	6.24803	2.17666	16.06	09.06
0.00775	6.49597	2.45622	15.51	08.54
0.00800	6.80188	2.79490	14.99	08.04

Table IV - Energies in a.u. of the Stark effect for the $n = 3$ six levels: (3,2,0,0), (3,0,2,0), (3,1,1,0), (3,1,0,1), (3,0,1,1) and (3,0,0,2) for various values of the field strength.

field (a.u)	(3,1,0,1) degree 15	(3,0,2,0) degree 15	(3,2,0,0) degree 15	(3,0,1,1) degree 15	(3,1,1,0) degree 15	(3,0,0,2) degree 10
0.0000	-.0555555	-.0555556	-.0555556	-.0555556	-.0555556	-.0555556
0.0001	-.0554226	-.0558220	-.0552886	-.0556894	-.0555563	-.0555624
0.0002	-.0552908	-.0560879	-.0550212	-.0558241	-.0555586	-.0555832
0.0003	-.0551598	-.0563533	-.0547533	-.0559597	-.0555624	-.0556178
0.0004	-.0550299	-.0566183	-.0544859	-.0560963	-.0555747	-.0556666
0.0005	-.0549009	-.0568828	-.0542159	-.0562338	-.0555831	-.0557300
0.0006	-.0547729	-.0571467	-.0539465	-.0563722	-.0555931	-.0558083
0.0007	-.0546460	-.0574103	-.0536766	-.0565114	-.0556046	-.0559021
0.0008	-.0545203	-.0576733	-.0534061	-.0566516	-.0556176	-.0560123
0.0009	-.0543951	-.0579360	-.0531351	-.0567926	-.0556322	-.0561400
0.0010	-.0542714	-.0579361	-.052836	-.0569345	-.0556679	-.0562867

Table V - Normalization constant, r-average and z-average values for various values of the field strength

field a.u.	normalization constant	r-average (a.u)	z-average (a.u.)
0.00000	$0.2871374836 \times 10^{03}$	2.0556	0.0000
0.00025	$0.2878496499 \times 10^{03}$	2.0636	0.0613
0.00050	$0.2900596446 \times 10^{03}$	2.0887	0.1261
0.00075	$0.2940157692 \times 10^{03}$	2.1346	0.1990
0.00100	$0.3002419652 \times 10^{03}$	2.2094	0.2878
0.00125	$0.3097640997 \times 10^{03}$	2.3296	0.4069
0.00130	$0.3122229568 \times 10^{03}$	2.3617	0.4366

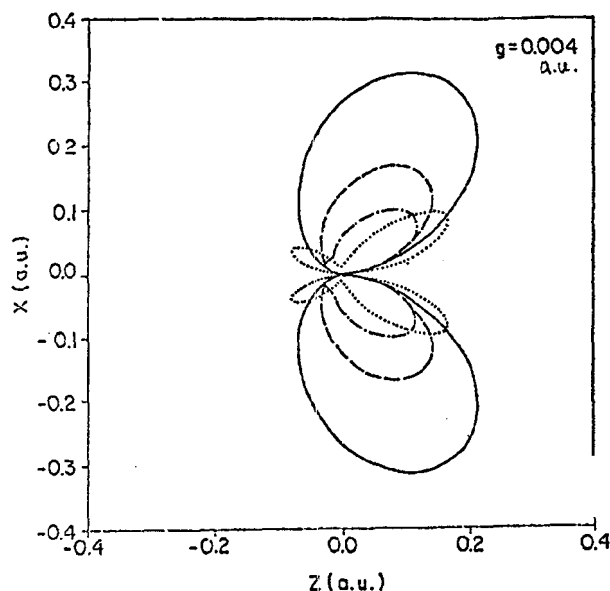


Figure 2: Same as Fig. 1 for the following values of r : 8.0 (—), 9.0 (— — —), 10.0 (- - - - -) and 12.0 (.....) for field $g = 0.004$ a.u. and same quantum numbers as in Fig. 1.

values of the radial distance the electronic density is only slightly stretched in the positive r -direction; as we increase the value of the radial distance, the electric multipole moments of greater order become apparent. This was expected in terms of what we have obtained in Table III. For a larger field, such that of Fig. 3 where $g = 0.006$ a.u. we can see that the effect of the field becomes apparent much sooner and gives rise to electric multipole moments of greater order.

For this second set of levels we also note that our scheme works well for lower field intensities as compared with the ground state¹⁶, the reason for this being that the $n = 2$ level is already delocalized and the action of a small field must increase the probability of autoionization. This occurs because the $n = 2$ level is already too delocalized and hence a small value for the field strength is sufficient to distort strongly the electronic wave function and to make the autoionization easier.

b) The $n = 3$ case:

For $n = 3$ and in the field free case we have a set of 9 degenerated levels. When the field is applied, the 9-fold degeneracy is partially broken into the following set of levels: (p_x, p_y) , (d_{xz}, d_{yz}) , $(d_{xz}, d_{x^2-y^2})$ and the remaining three single degenerate s , p_z and $d_{r^2-z^2}$. According to our previous notation these six new levels will be labeled as $(3,1,0,1)$, $(3,0,1,1)$, $(3,1,1,0)$, $(3,2,0,0)$, $(3,0,0,2)$ and $(3,0,2,0)$.

In Table IV we present the energies for the six levels and various values of the electric field with polynomial degrees of the order of 15. The convergence criterion adopted was the same as in the $n = 2$ case.

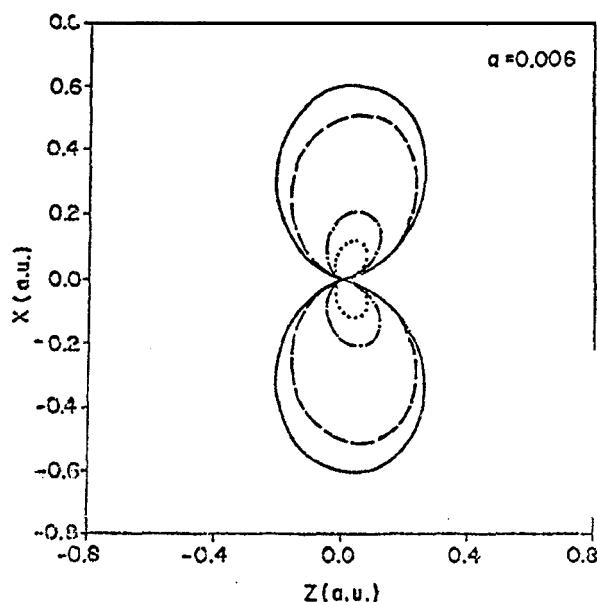


Figure 3: Same as Fig. 1 for the following values of r : 2.0 (—), 3.0 (— — —), 5.0 (- - - - -) and 6.0 (.....) for field $g = 0.006$ a.u. and same quantum numbers as in Fig. 1.

In Table V we present the results for an analysis of the case $(3,0,2)$ similar to that shown in Table III and one can see that the values of the dynamical variable r and r vary in the same way as before.

We point that in the $n = 3$ case the largest field strength for which we have calculated the eigenvalues was a factor of 6 smaller than that associated with the $n = 2$ case.

IV. Conclusions

The method here proposed can be extended to problems where the equations are not separable at all (hydrogen atom in presence of the laser field for example). In fact, some of the authors of the present work have already done such calculations for the Zeman effect¹⁸ and verified the same advantages pointed out in the present paper. We would like to point out that the proposed method is variational and so it represents a good estimate of the energies.

An advantage of the present method is the simplicity of its implementation. In fact, the calculations along this procedure can be performed even in a small computer at a reasonable speed, with the symmetry of the states taken into account from the beginning. Furthermore, when the results compared with those obtained by other methods (see Table I.b) the agreement found was quite satisfactory.

Acknowledgements

The authors wish to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)

for partial financial support and the LCC-FIS for the generous access to its computing facilities during the course of this work.

References

1. H. J. Silverstone, *Phys. Rev.* **18A**, 1853 (1978).
2. S. P. Alliluev, V. L. Eletsky, V. S. Popov and V. Rl. Weinberg, *Pliys. Lett.* **78A**, 43 (1980).
3. H. Noe, B. D. Etat and G. Couland, *Pliys. Lett.* **85A**, 327 (1981).
4. V. Rl. Weingerg, V. D. Mur, V. S. Popov and A. V. Sergeev, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 9 (1986).
5. V. S. Popov, V. M. Mur, A. V. Shcheblykin and V. Al. Weingerg, *Pliys. Lett.* **124A**, 77 (1987).
6. D. Bekenstein and J. B. Krieger, *Pliys. Rev.* **188**, 130 (1960).
7. J. A. C. Gallas and H. Walther, *Pliys. Rev.* **26A**, 1775 (1982).
8. M. H. Alexander, *Pliys. Rev.* **178**, **34** (1969).
9. R. J. Damburg and V. V. Kolorov, *J. Phys.* **B9**, 3149 (1979).
10. E. Luc-Koenig and A. Bachelier, *J. Pliys.* **1313**, 1743 (1980).
11. G. B. Hillard and W. L. Glab, *Physica* **145C**, 229 (1987).
12. V. V. Kolosov, *J. Phys.* **1320**, 2359 (1987).
13. I. W. Herbst, B. Siinon, *Pliys. Rev. Lett.* **41**, **G7** (1978); A. Magnet, Sliib I. Cliu, W. P. Reinhardt, *Phys. Rev.* **A27**, 2046 (1983); SI. Crance, *J. Opt. Soc. Ain.* **B7**, 449 (1990).
14. M. Klein, D. Robert, Xue Ping Wang, *Commun. Math. Pliys.* **131**, 109 (1990).
15. D. A. Telnov, *J. Pliys.* **B22**, 1309 (1989).
16. O. L. Silva Fillio, A. L. A. Fonseca, H. N. Nazareno and P. H. A. Guimarães, *Pliys. Rev.* **A42**, 4008 (1990).
17. O. L. Silva Filho, J. D. Rl. Vianna and A. L. A. Fonseca, *Pliys. Rev.* **A44**, 4717 (1001).
18. O. L. Silva Filho and A. L. **h** Fonseca, to be published.