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New method of perturbation-theory calculation of the Stark effect for the ground state of hydrogen

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Separation equations in parabolic coordinates are written in terms of the logarithmic derivative of the wave function. It is shown that for the ground state of the hydrogen Stark problem the nth order of the perturbation expansion is a polynomial of order n with integer coefficients. The energy coefficients, suitably defined, are integers and the calculation of the first 30 coefficients is listed.

Recently interest developed[1-5] in the formulation of perturbation theory in terms of the logarithmic derivative ψ'/ψ. For the one-dimensional Schrödinger equation a beautiful formalism was developed[1] by Aharonov and Au. This formalism is suited for the treatment of the ground and excited states (in Ref. 2 the method was rediscovered in a more limited form applicable, in fact, only for the ground-state perturbation expansion in one dimension).

The formulation of the perturbation theory in terms of the logarithmic derivative ("logarithmic gradient" $\nabla \log\psi$ in the multidimensional case[5]) has in some cases several advantages compared with the usual Rayleigh-Schrödinger formulas since the orders of the perturbation theory are expressed in quadratures.[1] This has a computational advantage and provides a method for deriving sum rules,[1] when compared with the usual expressions.

In this work we apply the ideas of Ref. 1–5 to the separation equations in parabolic coordinates for the ground-state Stark effect in hydrogen. We show that in this case the iteration formulas have a particularly simple structure.

The perturbation expansion for the Stark effect is in fact asymptotic.[6] Recent interest in high-order perturbative calculations[7] is connected with the discovery of asymptotic formulas[8] for the energy coefficients.

The calculation is performed[7] by two different methods.[9,10] The method presented here is more limited in that it is formulated only for the ground state. Nevertheless, in our formulation a considerable simplification of the iteration formulas and of the perturbation coefficients occurs. This provides an additional insight into the structure of the ground-state perturbation expansion and an alternative method for obtaining high-accuracy calculations.

The Schrödinger equation for the Stark effect in hydrogen (we use the units and the notation of Ref. 11),

$$(-\tfrac{1}{2}\nabla^2 - 1/r + \epsilon z)\Psi = E\Psi\,, \tag{1}$$

can be written in terms of the parabolic coordinates

$$\xi = r+z\,,\quad \eta = r-z\,,\quad \phi\,, \tag{2}$$

$$0 \le \xi,\quad \eta < \infty\,, \tag{3}$$

and by writing

$$\Psi = f(\xi)g(\eta)e^{im\phi} \tag{4}$$

the equation separates into

$$\frac{d}{d\xi}\left(\xi\frac{df}{d\xi}\right) + \left(\frac{E}{2}\xi - \frac{m^2}{4\xi} - \frac{\epsilon}{4}\xi^2\right)f + \beta_1 f = 0\,, \tag{5}$$

$$\frac{d}{d\eta}\left(\eta\frac{dg}{d\eta}\right) + \left(\frac{E}{2}\eta - \frac{m^2}{4\eta} + \frac{\epsilon}{4}\eta^2\right)g + \beta_2 g = 0\,, \tag{6}$$

where the separation constants β_1 and β_2 satisfy

$$\beta_1 + \beta_2 = 1\,. \tag{7}$$

Let

$$\alpha = (-2E)^{1/2} \tag{8}$$

and scale the variable in Eq. (5) [similarly for Eq. (6) with the opposite sign of ϵ] to

$$x = \alpha\xi\,,\quad 0 \le x < \infty\,. \tag{9}$$

The equation for the ground state ($m=0$) is

$$\frac{d}{dx}\left(x\frac{df}{dx}\right) + \left(B - \frac{x}{4} - Fx^2\right)f = 0\,, \tag{10}$$

where

$$B = \beta_1/\alpha\,, \tag{11}$$

$$F = \epsilon/4\alpha^3\,. \tag{12}$$

The perturbation expansion is constructed in the following steps:

(1) The perturbation expansion of $B(F)$ in powers of F is formulated using Eq. 10.

(2) The expansion of $\alpha^{-1}(\epsilon)$ in powers of ϵ is performed using the equation [compare Eq. (7)]

TABLE I. Separation constant coefficients.

n	a_n
0	1/2
1	2
2	-18
3	356
4	-10026
5	353004
6	-14648676
7	693735432
8	-36761448858
9	2151195801980
10	-137711887968492
11	9575504686567608
12	-719046899485503108
13	58031367405555829944
14	-5012509542203694355848
15	461645614244354685871632
16	-45180486910797811319287674
17	4684206984061422010138294428
18	-513012907550509477039708847772
19	59195631329111252630694903982296
20	-7179119706301814713183002277786860
21	913072070709127821783572945355025320
22	-121533909635472771173425818299653190520
23	16897488684933052311383111601054066856560
24	-2449707872392814528308365207148992682632996
25	369713055753950820054188629022072824627391256
26	-57998281861339927548667893429100513807262915256
27	9443928194302962265571498973632969648305050470192
28	-1594066304986358305260297895314351951189888861261768
29	2785755245475873556495919967440802433531185573427740000
30	-503458225572295251671053602081921642387487257250441840800
31	939939993078392213241159472711591757919164182066201019702400
32	-18109807210930545975626660311836249911188460794313762634529860
33	35974221293880959450664784599422753523600940691099411635438153200
34	-7361114686869058257814311621987307639100889238645861003813642585200
35	15502545167023365927841614107492535921347538977083799982999519207960
36	-3357549584538820232821873447925830830368371361768920298633285241367644
37	74726251445939867422609039138237996922158830068046407796171690488336724000
38	-1707826476590121951067499466916865491946501675933581420107934860560532334320
39	400533054621788231842270160321563985089495188225115538806071743064842531032800
40	-963332089855088537405757077700424846574822055608957270547672214509315863406030000
41	23745937899759078681484274408616621626888499956955526057467485805948037222180760400
42	-599547394807877013291931801823547924276980254641111989649833394126944030862753898536
43	15496572629683584658976092996626845657160647225633670999158804726507063301677825366952000
44	-40982060222724541565554046273499879528887383802873585398953505287454981383590744114854584
45	110834825338974163126798562751031196129662315136613291252143541270084754779950360362217853600
46	-3063874404540358638173518903884286079262564295274730

TABLE I. (*Continued.*)

n	a_n
	5794268039847462785574292363739423122158960
47	8653162995055989563853604336697993939269527692199800
	01959946685951155135666527910369526872260016О
48	-249570592754300583509042814447297603882248807145697
	08018544187238664815721401210134183417339589258O
49	7347504527225482704819875766722973872318172549164133
	8283483629144736991091795844282559780467662675160
50	-220716614416936069788916533074476185493087572020864
	0866287051497572412522328134111393839599961937O700
	120
51	6762491177286608958304158063044409146176339738887666
	676133704460647235111905326404849616260290441028955
	888
52	-211246416804644337079194648099980255406876791245915
	1028588925013221262997610199184841982388614833961801
	256888
53	6725485254600440693901387286469780864015079575822061
	4593429471322289657154615240546662013650654185278505
	3528464
54	-218150451237966894934068694587268675342470031733346
	0440756595818555019564120999479317823404029233597467
	1642144O688
55	7206742227848342826113517358477583418335309931130898
	7850827217211114475691267407719516798805348278473486
	368800882784
56	-242398368256182231870199748637510423052828592899520
	1800925534194490675786307807995785717180989031270650
	4446112642073096
57	8298329626335159887094231431511722859046426171418707
	4319736134097896201099005201884604005867602569605639
	95481396950441648
58	-289060774519208464859165159381851080310610894581233
	8793138827273634565729700443328610464110670067554537
	7430140521374242480048
59	1024228470341297028526154540177091767400289301799002
	9422808476094949422448639337674939582330937361563079
	57947294495858137697632
60	-369053833445722593964532876340158035439273185619911
	3284994651839672535875713907068153595150008146449565
	73076134464716786684897936

$$B\left(\frac{\epsilon}{4\alpha^3}\right)+B\left(-\frac{\epsilon}{4\alpha^3}\right)=\frac{1}{\alpha}. \tag{13}$$

(3) The expansion of $E(\epsilon)$ in powers of ϵ is found using

$$E(\epsilon)=-\tfrac{1}{2}\alpha^2(\epsilon). \tag{14}$$

To formulate the perturbation expansion of Eq. (10) we rewrite it in terms of the logarithmic derivative

$$y=f'/f, \tag{15}$$

$$x(y'+y^2)+y=-B+\tfrac{1}{4}x+Fx^2. \tag{16}$$

Before proceeding let us mention that the relevant solution of Eq. (10) with zero field

$$\frac{d}{dx}\left(x\frac{df_0}{dx}\right)+\left(B_0-\frac{x}{4}\right)f_0=0 \tag{17}$$

is

$$B_0=\tfrac{1}{2},\ f_0\propto e^{-x/2}. \tag{18}$$

To derive the perturbation theory equations we substitute

$$B=\sum_{n=0}^{\infty}a_nF^n,\quad a_0=\tfrac{1}{2}, \tag{19}$$

$$y=\sum_{n=0}^{\infty}y_nF^n,\quad y_0=-\tfrac{1}{2}, \tag{20}$$

in Eq. (16) and equate the powers of F.

The first-order equation is

$$x(y_1'-y_1)+y_1=-a_1+x^2, \tag{21}$$

with the solution (regular at $x=0$)

$$a_1=\int_0^{\infty} x^2 e^{-x}dx=2\,, \tag{22}$$

$$-y_1=\frac{e^x}{x}\int_x^{\infty}(x^2-a_1)e^{-x}dx=x+2\,. \tag{23}$$

The kth-order equation for $k\geq 2$ is

$$x(y_k'-y_k)+y_k=-a_k-x\sum_{n=1}^{k-1}y_n y_{k-n}\,, \tag{24}$$

with the solution (regular at $x=0$)

$$a_k=-\int_0^{\infty} x e^{-x}\sum_{n=1}^{k-1}y_n y_{k-n}dx\,,\quad k\geq 2 \tag{25}$$

$$-y_k=-\frac{e^x}{x}\int_x^{\infty}\left(a_k+x\sum_{n=1}^{k-1}y_n y_{k-n}\right)e^{-x}dx\,,\quad k\geq 2\,. \tag{26}$$

The following properties of the functions y_k and the coefficients a_k are proved easily by induction:

TABLE II. Energy coefficients.

n	e_n
0	1
1	72
2	28440
3	40204464
4	10410222424
5	407963089956240
6	2223418553147644656
7	16065831970607635384416
8	149009341926825814343301720
9	1730459956788066582386297858256
10	24652334211653276351335413061052496
11	423394456043937653108555199936028061088
12	8636079472084569706063332857736009200480496
13	206508654866625082411378314631895980291649441184
14	5724105464556914136546941338673284622148688788141792
15	1821111253106244923276209200965333449090144254623043 96480
16	6592527588322967457062262219175635563242670128726810 186767960
17	2694726486739955058296768160555100007195533894424668 95243008790864
18	1235240423690124581026672767067143288085723118995321 8039275915016404112
19	6311030314276808304549968877721662697298766944474293 23840413125403432316192
20	3574084638661177195359113566223317259515245791213620 8006251196906540225891808848
21	2232429795935428501626676610458801022143265114004238 412647622523912709399665552360672
22	1530981220327305447017106017433429268506073399858351 37202768994927738925611823507863946016
23	1148005899938852004250776074678927729330313602693568 9756663736384103252812644586140109549389120
24	9376801674837581408509435064697002924719337083571292 57177202933996252429022807487391363438236110064
25	8313593557890761469877582537593693123123620480431348 3540809193160806301254619412504458873667928393330464
26	7975372759680899748810249108523949932544942788203011 8081093164755690061249180140002013615620174214777222 67936
27	8253735433136293648022396954191871796243897884818419 4830323286727125921611846114751296623156901802660545 6802246720
28	9189458675439933313362818814383488677157764323607952 1105386902494198303813188440624893642018814051832328 196649614996192
29	1097880843208513078546995442513224472886731865347297 9309368948683326145979185071246147890563125731804212 41361213348133100 4736
30	1404130952009071441845392842905456764561573839406225 4411647983989461840909913153920582574464643776416776 51225860683352276020392384

(1) a_k ($k \geq 1$) is an integer number; (2) y_k ($k \geq 1$) is a polynomial of power k with integer coefficients.

In Table I we list 60 first coefficients a_k, the first few polynomials y_k are

$$-y_2 = -x^2 - 7x - 18\,, \qquad (27)$$

$$-y_3 = 2x^3 + 26x^2 + 142x + 356\,, \qquad (28)$$

$$-y_4 = -5x^4 - 99x^3 - 869x^2 - 4139x - 10\,026\,, \qquad (29)$$

$$-y_5 = 14x^5 + 382x^4 + 4764x^3 + 34\,446x^2 + 150\,042x + 353\,004\,. \qquad (30)$$

As the next step, we calculate the coefficients c_n in the series

$$\frac{1}{\alpha} = \sum_{n=0}^{\infty} c_n \left(\frac{\epsilon}{4}\right)^{2n}, \quad c_0 = 1 \qquad (31)$$

with the aid of Eq. (13) [only even-order coefficients a_n of the expansion of Eq. (19) contribute due to the form of Eq. (13)].

Finally, the coefficients e_n in the series

$$E = -\tfrac{1}{2} \sum_{n=0}^{\infty} e_n \left(\frac{\epsilon}{4}\right)^{2n}, \quad e_0 = 1\,, \qquad (32)$$

are calculated using Eq. (14). It is easy to prove that the coefficients c_n and e_n in Eqs. (31) and (32) are integer numbers. The first 30 coefficients e_n are listed in Table II.

The results of the proceeding discussion demonstrate the advantages of the formulation of perturbative expansions in terms of the logarithmic derivative $(\log\psi)'$ in the one-dimensional case[1] or the "logarithmic gradient" $\vec{\nabla}\log\psi$ in the multidimensional case.[5] For the ground state $(\log\psi)'$ is expected to be a smooth, well-behaved function and there is a hope that the terms of the perturbation theory have a simple structure (in our case—polynomials). Finally, let us mention that Eq. (16) may be of interest in nonperturbative studies of the Stark effect for the ground state of hydrogen.

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[1] Y. Aharonov and C. K. Au, Phys. Rev. Lett. 42, 1582 (1979).
[2] A. V. Turbiner, Zh. Eksp. Teor. Fiz. Pis'ma Red. 30, 379 (1979). (JETP Lett.) (to be published).
[3] S. Hikami and E. Bresin, J. Phys. A 12, 759 (1979).
[4] A. D. Dolgov and V. S. Popov, Zh. Eksp. Teor. Fiz. 75, 2010 (1978) [Sov. Phys.-JETP 48, 1012 (1978)].
[5] V. Privman (unpublished).
[6] E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second-Order Differential Equations* (Oxford University Press, London, 1958), 2nd ed., Chap. 20.
[7] H. J. Silverstone, B. G. Adams, J. Cizek, and P. Otto, Phys. Rev. Lett. 43, 1498 (1979).
[8] I. W. Herbst and B. Simon, Phys. Rev. Lett. 41, 67 (1978) and references therein.
[9] H. J. Silverstone, Phys. Rev. A 18, 1853 (1978).
[10] M. Bednar, Phys. Rev. A 15, 27 (1977); J. Cizek and J. Paldus, Int. J. Quantum Chem. 12, 875 (1977).
[11] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Pergamon, New York, 1977), 3rd ed., Chap. X.