Transcendental-function representation of Stark-modified hydrogenic states and atomic dipole polarizability

Transcendental-function representation of Stark-modified hydrogenic states and atomic dipole polarizability

A Bhattacharya†, B Talukdar†, G Banerji‡ and U Roy§

† Department of Physics, Visva-Bharati University, Santiniketan-731235, India
‡ Mathematics Department, BU, Burdwan, India
§ Theoretical Physics Department, IACS, Calcutta-700032, India

Abstract. A differential equation approach to the perturbation theoretic correction for excited hydrogenic states is introduced. The radial equations for the problem are solved in terms of known transcendental functions and the method to determine the complete primitive is discussed. The constructed perturbative correction to the wavefunction is adapted to evaluate the dipole polarizability of hydrogenic atoms.

1. Introduction

The displacement of energy levels of an atom placed in a static homogeneous electric field E goes by the name Stark effect and is calculated by using perturbation theory provided E is weak enough to produce energy shifts which are small compared with the distances between neighbouring energy levels of the atom, including the fine structure interval. The quadratic Stark effect is closely related with the induced dipole polarizability [1]. It is not convenient to use the Rayleigh–Schrödinger perturbation theory (RSPT) [2] to calculate this quadratic effect since it would then be necessary to deal with infinite sums of complicated form [3]. Instead, it is easier to work with a simple variant [4] of the RSPT in which the perturbation corrections to wavefunctions are obtained from the solution of nonhomogeneous differential equations. Because of our interest in the dipole polarizability we shall restrict ourselves only to the first-order correction to the wavefunction.

Let H be the Hamiltonian of the perturbed system written as

$$H = H_0 + \lambda H'. \tag{1}$$

Here H_0 stands for the solvable Hamiltonian of the unperturbed system and H' is a small perturbation over H_0 with a coupling constant λ. In the differential equation approach noted above the eigenket $|\psi_1\rangle$ for the first-order correction to the unperturbed eigenket $|\psi_0\rangle$ satisfies the inhomogeneous equation

$$(E_0 - H_0)|\psi_1\rangle = H'|\psi_0\rangle - |\psi_0\rangle\langle\psi_0|H'|\psi_0\rangle \tag{2}$$

with

$$H_0|\psi_0\rangle = E_0|\psi_0\rangle. \tag{3}$$

It is well known that for $H' = Er\cos\theta$, the equation in (2) can be solved for $|\psi_1\rangle$ when E_0 is nondegenerate. Throughout this paper we shall use Hartree atomic units. The expression

for $|\psi_1\rangle$ when used to calculate the second-order perturbed energy for the ground state of the hydrogen atom gives an exact value for the dipole polarizability. In the presence of degeneracy, the solution of (2) is obstructed by the solvability condition [5]. Thus, the treatment of the excited states of hydrogen and hydrogen-like atoms by the differential equation approach needs a separate consideration. Fortunately, the solvability condition of (2) for dealing with perturbative corrections to degenerate states can be satisfied by replacing $|\psi_0\rangle\langle\psi_0|$ by $\sum_{\gamma\in\text{degenerate subspace}}|\psi_\gamma\rangle\langle\psi_\gamma|$ [6]. This replacement is equivalent to multiplying H' by projection operators that exclude degenerate-state contributions [7]. Thus, the appropriate inhomogeneous equation that can be used to obtain the first-order correction to wavefunctions belonging to a degenerate energy level is given by

$$(E_0 - H_0)|\psi_1\rangle = H'|\psi_0\rangle - \sum_\gamma |\psi_\gamma\rangle\langle\psi_\gamma|H'|\psi_0\rangle. \tag{4}$$

The representation-space version of (4) has been used by Jhanwar and Meath [8] and Au [7] to calculate dipole and multipole polarizabilities for hydrogenic bound states.

In this work we wish to solve the inhomogeneous equation in (4) in terms of known transcendental functions and thereby supplement the series-integration method [7, 8] which requires the use of certain complicated recurrence relations. The solutions obtained by us refer to a hydrogenic atom placed in a constant electric field and, as we shall see, are very useful to calculate dipole polarizabilities for arbitrary hydrogenic states. In section 2 we take the projection of (4) into the r-space and carry out the separation of variables. If the perturbation is a homogeneous electric field the r-space equation decomposes naturally into two uncoupled radial equations because of the dipole parity selection rule. Further, we note that these two equations could also be written as a single equation. In section 3 we relate these radial equations to a nonhomogeneous differential equation for the confluent hypergeometric function given in Babister [9] and obtain their solutions in terms of known transcendental functions. Since the dipole polarizability has the form of a second-order perturbed energy, in section 4 we use the results for correction to the wavefunction to compute numbers for dipole polarizabilities of highly excited hydrogenic bound states and present some concluding remarks.

2. Operator equation (4) in the representation space

As a first step to derive a physico-mathematical method for the solution of (4), we take its projection in the r-space. This gives

$$(E_0 - H_0(r))\psi_1(r) = H'(r)\psi_0(r) - \sum_\gamma \psi_\gamma(r)\int \psi_\gamma(r')H'(r')\psi_0(r')\,\mathrm{d}^3r'. \tag{5}$$

In (5), $H_0(r)$ involves the appropriate Coulomb interaction for a Z-electron atom. Obviously,

$$\psi_0(r) = R_{n,l}(r)Y_l^m(\theta, \phi). \tag{6}$$

Here $Y_l^m(\theta, \phi)$ stands for the scalar spherical harmonic and $R_{n,l}(r)$ stands for the bound-state solution of the Coulomb problem given by,

$$R_{n,l}(r) = N_{n,l}\rho^l \mathrm{e}^{\frac{-\rho}{2}} L_{n-l-1}^{2l+1}(\rho) \tag{7}$$

with

$$N_{n,l} = \left[\frac{4Z^3(n-l-1)!}{n^4(n+l)!}\right]^{\frac{1}{2}}. \tag{8}$$

In (7) $L_s^k(\cdot)$ stands for the associated Laguerre polynomial of order s and $\rho = \frac{2Zr}{n}$. Because of our interest in atomic polarizabilities for arbitrary values of (n, l) we take $H'(\mathbf{r}) = z = r\cos\theta$. Since H' can connect only the states of opposite parity, we choose the solution of (5) in the form

$$\psi_1(\mathbf{r}) = F_{n,l}(r)Y_{l-1}^m(\theta, \phi) + G_{n,l}(r)Y_{l+1}^m(\theta, \phi). \tag{9}$$

We now implement the dipole selection rule, perform the sum over degenerate states and carry out the separation of variables. We thus obtain, from (5) the following radial equations

$$\left[\rho\frac{d^2}{d\rho^2} + 2\frac{d}{d\rho} - \frac{\rho}{4} + n - \frac{l(l-1)}{\rho}\right]F_{n,l}(\rho)$$
$$= \frac{n^2\rho}{2Z^2}A(l, m)[\rho R_{n,l} + B(n, l)R_{n,l-1}] \qquad l \geqslant 1 \tag{10}$$

and

$$\left[\rho\frac{d^2}{d\rho^2} + 2\frac{d}{d\rho} - \frac{\rho}{4} + n - \frac{(l+1)(l+2)}{\rho}\right]G_{n,l}(\rho)$$
$$= \frac{n^2\rho}{2Z^2}A(l+1, m)[\rho R_{n,l} + B(n, l+1)R_{n,l+1}] \qquad l \geqslant 0 \tag{11}$$

with

$$A(l, m) = \left[\frac{l^2 - m^2}{(2l-1)(2l+1)}\right]^{\frac{1}{2}} \tag{12}$$

and

$$B(n, l) = \frac{3n^5 N_{n,l} N_{n,l-1}(n+l)!}{8Z^4(n-l-1)!}. \tag{13}$$

The solutions of (10) and (11) are subject to the constraint

$$\langle\psi_0|\psi_1\rangle = 0. \tag{14}$$

Au [7] found that the uncoupled equations for $F_{n,l}(r)$ and $G_{n,l}(r)$ could be represented by a single inhomogeneous differential equation by assuming

$$\psi_1(\mathbf{r}) = N_{n,l}e^{-\frac{r}{n}}\sum_j R_j(r)\alpha_j(1, l)Y_j^0 \tag{15}$$

where $\alpha_j(1, l)$ represents the usual vector coupling coefficient given by

$$\alpha_j(1, l) = \sqrt{(2l+1)(2j+1)}\begin{pmatrix} 1 & l & j \\ 0 & 0 & 0 \end{pmatrix}. \tag{16}$$

The radial function $R_j(r)$ satisfies the inhomogeneous differential equation

$$r\frac{d^2}{dr^2}(rR_j) - j(j+1)R_j - \frac{2r^2}{n}\frac{d}{dr}R_j + \frac{2(n-1)}{n}rR_j$$
$$= 2\left(\frac{2}{n}\right)^\lambda \sum_{k=0}^{n-l-1} \frac{(n-l-1)_k}{(2l+2)_k}\left(\frac{2}{n}\right)^k r^{l+k+3} \tag{17}$$

with the Pochhammer symbol

$$(\alpha)_i = \frac{\Gamma(\alpha+i)}{\Gamma(\alpha)}. \tag{18}$$

The solution of (17) in conjunction with (18) through the triangular condition on the 3-j symbol involved in (16) reproduces the combination in (9) such that the equivalence between

the approach of Jhanwar and Meath [8] and that of Au [7] is obvious. In the following we deal with the nonhomogeneous equations in (10) and (11) and relate them with well known transcendental equations studied by Babister [9]. Admittedly, one would like to regard such a viewpoint as more systematic and an improvement over the power series solution tried earlier.

3. Transcendental-function representation of $F_{n,l}(\rho)$ and $G_{n,l}(\rho)$

The functions $F_{n,l}(\rho)$ and $G_{n,l}(\rho)$ satisfy nonhomogeneous linear second-order differential equations given in (10) and (11). We now show that their associated homogeneous equation is the confluent hypergeometric equation given by

$$x\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + (c - x)\frac{\mathrm{d}y}{\mathrm{d}x} - ay = 0 \tag{19}$$

where a and c are constants. The theory of confluent hypergeometric equations is fully set out in Buchholz [10] and Erdelyi [11]. However, for our use we note that the two independent solutions of (19) are given by

$$y_1 = {}_1F_1(a; c; x) = \frac{\Gamma(c)}{\Gamma(a)}\sum_{n=0}^{\infty}\frac{\Gamma(a+n)}{\Gamma(c+n)}\frac{x^n}{n!} \tag{20}$$

and

$$y_2 = x^{1-c}\,{}_1F_1(a - c + 1; 2 - c; x). \tag{21}$$

The results in (20) and (21) are referred to as the regular and irregular confluent hypergeometric functions. Because of physical boundary conditions only involved the ${}_1F_1(.)$ functions will enter as the complementary functions in the solutions of (10) and (11) and the complete primitive will be found out accordingly.

We now change the dependent variables in (10) and (11) by substituting

$$F_{n,l}(\rho) = \rho^{l-1}\mathrm{e}^{-\frac{\rho}{2}}M(\rho) \tag{22}$$

and

$$G_{n,l}(\rho) = \rho^{l+1}\mathrm{e}^{-\frac{\rho}{2}}N(\rho) \tag{23}$$

where $M(\rho)$ and $N(\rho)$ are polynomials in ρ. For the sake of brevity we omit the subscripts n and l in the right-hand side of (22) and (23). From (10), (11), (22) and (23) we obtain,

$$\rho M'' + (2l - \rho)M' + (n - l)M = \frac{n^3 A(l, m)N_{n,l}}{4z^3}$$
$$\times \sum_{j=0}^{n-l-1}\left[(-1)^j\frac{(n+l)!}{j!(n-l-1-j)!(2l+j)!}\right.$$
$$\left.\times\left\{\frac{\rho^{3+j}}{(2l+j+1)} - 3\rho^{2+j} + 3(2l+j)\rho^{1+j}\right\}\right] \tag{24}$$

and

$$\rho N'' + (2l + 4 - \rho)N' + \{n - (l+2)\}N = \frac{n^3 A(l+1, m)N_{n,l}}{4Z^3}$$
$$\times \sum_{j=0}^{n-l-1}\left[(-1)^j\frac{(n+l)!\rho^{j+1}}{j!(n-l-1-j)!(2l+j+1)!}\right.$$

$$\times \left\{ 1 + \frac{3(n + l + 1)(n - l - 3)}{(2l + j + 2)(2l + j + 3)} \right\} \right]. \tag{25}$$

In writing (24) and (25) we have also used (7) with the well known expression for associated Laguerre polynomial.

Since the right-hand sides of these equations involve finite sum, their solutions can be related to the solution of nonhomogeneous confluent hypergeometric equation

$$x \frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + (c - x) \frac{\mathrm{d}y}{\mathrm{d}x} - a y = x^{\sigma - 1} \tag{26}$$

where σ is a constant. Thus we have

$$M(\rho) = C_{M1} F_1(l - n; 2l; \rho) + \frac{n^3 A(l, m) N_{n,l}}{4Z^3}$$
$$\times \sum_{j=0}^{n-l-1} \left[(-1)^j \frac{(n + l)!}{j!(n - l - 1 - j)!(2l + j)!} \right.$$
$$\left. \times \left\{ \frac{\theta_{j+4}(l - n, 2l; \rho)}{(2l + j + 1)} - 3\theta_{j+3}(l - n, 2l; \rho) + 3(2l + j)\theta_{j+2}(l - n, 2l; \rho) \right\} \right] \tag{27}$$

and

$$N(\rho) = C_{N1} F_1(l + 2 - n; 2l + 4; \rho) + \frac{n^3 A(l + 1, m) N_{n,l}}{4Z^3}$$
$$\times \sum_{j=0}^{n-l-1} \left[(-1)^j \frac{(n + l)!}{j!(n - l - 1 - j)!(2l + j + 1)!} \right.$$
$$\left. \times \left\{ 1 + \frac{3(n + l + 1)(n - l - 1 - j)}{(2l + j + 2)(2l + j + 3)} \right\} \theta_{j+2}(l + 2 - n, 2l + 4; \rho) \right] \tag{28}$$

with C_M and C_N as the constants of integration. The quantity $\theta_j(\cdot)$ is expressed in terms of generalized hypergeometric function as

$$\theta_\sigma(a, c; x) = \frac{x^\sigma}{\sigma(\sigma + c - 1)} {}_2F_2(1, \sigma + a; \sigma + 1, \sigma + c; x). \tag{29}$$

From (22), (23), (27) and (28) we obtain

$$F_{n,l}(\rho) = \rho^{l-1} \mathrm{e}^{-\frac{\rho}{2}} \left[C_{M1} F_1(l - n; 2l; \rho) + \frac{n^3 A(l, m) N_{n,l}}{4Z^3} \right.$$
$$\times \sum_{j=0}^{n-l-1} \left[(-1)^j \frac{(n + l)!}{j!(n - l - 1 - j)!(2l + j)!} \right.$$
$$\left. \left. \times \left\{ \frac{\theta_{j+4}(l - n, 2l; \rho)}{(2l + j + 1)} - 3\theta_{j+3}(l - n, 2l; \rho) + 3(2l + j)\theta_{j+2}(l - n, 2l; \rho) \right\} \right] \right]$$
$$l \geqslant 1 \tag{30}$$

and

$$G_{n,l}(\rho) = \rho^{l+1} \mathrm{e}^{-\frac{\rho}{2}} \left[c_{N1} F_1(l + 2 - n; 2l + 4; \rho) + \frac{n^3 A(l + 1, m) N_{n,l}}{4Z^3} \right.$$
$$\times \sum_{j=0}^{n-l-1} \left[(-1)^j \frac{(n + l)!}{j!(n - l - 1 - j)!(2l + j + 1)!} \right.$$

$$\times \left\{ 1 + \frac{3(n+l+1)(n-l-1-j)}{(2l+j+2)(2l+j+3)} \right\} \theta_{j+2}(l+2-n, 2l+4; \rho) \right]\right]$$

$$l \geqslant 0. \tag{31}$$

For given values of n and l the functions $\theta_j(\cdot)$ occurring in (27) and (28) can be written in terms of elementary functions by using the recurrence relation

$$(\sigma + a)\theta_{\sigma+1}(a, c; x) = \sigma(\sigma + c - 1)\theta_\sigma(a, c; x) - x^\sigma. \tag{32}$$

We also require the use of the following [9, 10].

$$\theta_\sigma(1, c; x) = \frac{x^\sigma}{\sigma(\sigma + c - 1)} \, {}_1F_1(1; \sigma + c; x) \tag{33}$$

and

$$z \, {}_1F_1(a; b+1; z) = b[\, {}_1F_1(a; b; z) - \, {}_1F_1(a-1; b; z)]. \tag{34}$$

Some remarks on fixing the values of C_M and C_N are now in order. The quantity $(l-n)$ is always a negative integer such that the $_1F_1(\cdot)$ function in (30) is always a polynomial. On the other hand, in addition to taking up possible negative integral values, the quantity $(l+2-n)$ can also be 0 and 1. In general, C_M and C_N are determined from the orthogonality relation in (14) which, in view of (9), decomposes into two radial equations

$$\int_0^\infty R_{n,l-1}(r)F_{n,l}(r)r^2 \, \mathrm{d}r = 0 \qquad \text{and} \qquad \int_0^\infty R_{n,l+1}(r)G_{n,l}(r)r^2 \, \mathrm{d}r = 0. \tag{35}$$

When $l+2-n = 1$, the $_1F_1(\cdot)$ function in (31) becomes an infinite series which diverges asymptotically. In this case we have found that some multiple (say δ) of the same hypergeometric function occurs in the inhomogeneous part of (31) in addition to a well-behaved polynomial part obtained by repeated application of the recurrence relation in (32). The asymptotic boundary condition is then satisfied by setting $(C_N + \delta) = 0$. This is the standard route one should follow to construct the expression for $G_{n,l}(\rho)$ when $l+2-n = 1$. In the next section we use (30) and (31) to calculate atomic polarizabilities for degenerate bound states. This gives us an opportunity to explicitly demonstrate the algebraic procedure to be followed to obtain results for C_M and C_N and $\theta_\sigma(a, c; z)$.

4. Polarizabilities for hydrogenic bound states

The expression for polarizability for an arbitrary bound state (n, l, m) is given by [6]

$$\alpha(n, l, m) = -2 \int \psi_0(r) r \cos\theta \psi_1(r) \, \mathrm{d}^3 r. \tag{36}$$

From (6), (9) and (36) we can write

$$\alpha(n, l, m) = \alpha_1(n, l, m) + \alpha_2(n, l, m) \tag{37}$$

with

$$\alpha_1(n, l, m) = -2 \int_0^\infty r^3 R_{n,l}(r)F_{n,l}(r) \, \mathrm{d}r \int Y_l^{m\star}(\theta, \phi) \cos\theta Y_{l-1}^m(\theta, \phi) \, \mathrm{d}\Omega \tag{38}$$

and

$$\alpha_2(n, l, m) = -2 \int_0^\infty r^3 R_{n,l}(r)G_{n,l}(r) \, \mathrm{d}r \int Y_l^{m\star}(\theta, \phi) \cos\theta Y_{l+1}^m(\theta, \phi) \, \mathrm{d}\Omega. \tag{39}$$

For numerical evaluation of polarizabilities one will require the values of C_M and C_N beforehand. We deal with this for a particular value of the principal quantum number.

We calculate the constants of integration in (30) and (31) for $n = 4$. Here l can vary from 0 to 3. For $n = 4$ and $l = 3$, (30) gives

$$F_{4,3}(r) = \frac{(Zr)^2}{4} e^{-\frac{Zr}{4}} \left[C_M \left(1 - \frac{Zr}{12} \right) + \frac{A(3, m)}{6\sqrt{35} Z^{\frac{3}{2}}} \left(\frac{(3Zr)^2}{4} - \frac{(Zr)^3}{16} \right) \right]. \tag{40}$$

In writing (40) we have made iterative use of the recurrence relation in (32). Using (40) in the first orthogonality condition given in (35) we obtain

$$C_M = \frac{9\sqrt{\frac{7}{5}} A(3, m)}{Z^{3/2}}. \tag{41}$$

Similar iterative use of (32) gives

$$G_{4,3}(r) = \frac{(Zr)^4}{16} e^{-\frac{Zr}{4}} \left[\left\{ C_N + \frac{5A(4, m)}{6\sqrt{35} Z^{3/2}} \right\} {}_1F_1 \left(1; 10; \frac{Zr}{2} \right) - \frac{A(4, m)}{12\sqrt{35} Z^{3/2}} \left(10 + \frac{Zr}{2} \right) \right]. \tag{42}$$

In the derivation of (42) we have also used the three-term recurrence relation in (34). The function ${}_1F_1(1, 10; \frac{Zr}{2})$ in (42) violates the asymptotic boundary condition for $G_{4,3}(r)$. We circumvent this by demanding that the quantity in the curly brackets is zero and finally obtain

$$G_{4,3}(r) = -\frac{(Zr)^4}{16} e^{-\frac{Zr}{4}} \frac{A(4, m)}{12\sqrt{35} Z^{3/2}} \left(10 + \frac{Zr}{2} \right). \tag{43}$$

The result for the integration constant in $F_{4,2}$ can be obtained by using the same procedure as was done for $F_{4,3}(r)$. However, evaluation of C_N for $G_{4,2}(r)$ can be done in a straightforward way from only second orthogonality condition in (35) and one need not take recourse to the use of asymptotic boundary condition, whatsoever. In general, we have found that the constants in $F_{n,l}(r)$ and $G_{n,l}(r)$ are determined by the conditions in (35) with the only exception for that of $G_{n,l}(r)$ in the ground state of the spectral series, i.e. $l = n - 1$.

Finally, we used the values of F and G to obtain numbers for polarizabilities of the hydrogen atom. It is important to note that calculation of $\alpha_1(\cdot)$ and $\alpha_2(\cdot)$ from (38) and (39) involved only elementary integrals. Table 1 gives these results as a function of l and n.

These results show that for a given value of n, the polarizability α increases as l increases and for fixed l the number decreases with m. This can be understood easily by using the graphic language of Bohr. In the presence of an electric field the quantum orbits are disturbed and the disturbance affects the various ellipses differently. The deformation in the circular orbit appears to be more pronounced and it decreases gradually as the eccentricity of the ellipse increases. This results in the behaviour of the numbers presented in table 1. The use of our wavefunctions to compute values of α for arbitrary n is quite straightforward.

Table 1. Dipole polarizabilities in au of the hydrogen atom for $n = 4$.

		m		
l	0	±1	±2	±3
0	4 992			
1	7 449.6	5 107.2		
2	9 600	8 640	5 760	
3	13 286.4	12 556.8	10 368	6720

We, therefore, conclude by noting that our treatment of the Dalgarno–Lewis technique for degenerate states represents an improvement over the power series and partial-wave techniques discussed earlier [8, 7].

Acknowledgments

References

[1] Friedrich H 1991 *Theoretical Atomic Physics* (New York: Springer)
[2] Schiff L I 1968 *Quantum Mechanics* (Tokyo: McGraw-Hill, Kogakusha Ltd)
[3] Mavromatis H A 1991 *Am. J. Phys.* **59** 738
[4] Dalgarno A and Lewis J T 1955 *Proc. R. Soc.* A **233** 70
[5] Nayfeh A H 1981 *Introduction to Perturbation Techniques* (New York: Wiley)
[6] Adamov M N, Kagen B K and Orlov B I 1965 *Opt. Spectrosc.* **19** 171
     Adamov M N, Balmakov M D and Rebane T K 1969 *Opt. Spectrosc.* **27** 100
     Marinescu M and Dalgarno A 1995 *Phys. Rev.* A **52** 311
[7] Au C K 1984 *Phys. Rev.* A **29** 1034
[8] Jhanwar B L and Meath W J 1980 *Mol. Phys.* **40** 713
[9] Babister A W 1967 *Transcendental Functions Satisfying Nonhomogeneous Linear Differential Equations* (New York: Macmillan)
[10] Buchholz H 1969 *The Confluent Hypergeometric Functions* (New York: Springer)
[11] Erdelyi A 1953 *Higher Transcendental Functions* vol 1 (New York: McGraw-Hill)
     Erdelyi A 1954 *Higher Transcendental Functions* vol 2 (New York: McGraw-Hill)