Large-order perturbation theory without a wavefunction for the LoSurdo–Stark effect in hydrogenic atoms

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Abstract. I obtain exact large-order perturbation corrections to the energy shifts of the LoSurdo-Stark effect in hydrogenic atoms for both non-degenerate and degenerate states. The method consists of applying perturbation theory to a recurrence relation among properly selected moments of the eigenfunction which do not explicitly appear in the calculation. The resulting recurrence relation for the perturbation corrections is suitable for computer algebra calculation of perturbation corrections to the energy. The method is most useful to treat both separable and non-separable problems in any convenient coordinate system. Here I use spherical polar coordinates and calculate the shifts of the first two hydrogenic energy levels as illustrative examples.

1. Introduction

The LoSurdo–Stark effect in hydrogen was the first problem treated by means of quantum mechanical perturbation theory [1]. Since then, many authors have developed improved techniques for obtaining more perturbation corrections. Because the Schrödinger equation is separable in parabolic coordinates one can avoid the use of perturbation theory for degenerate states. The resulting pair of one-dimensional eigenvalue equations in such coordinates have been treated in many different ways: straightforward integration of the hierarchy of Rayleigh-Schrödinger perturbation equations by means of hypergeometric functions [2], expansions of the solutions in Taylor series [3] or series of Laguerre polynomials [4], transformation of the linear eigenvalue equations into Riccati equations for the derivatives of the logarithm of the eigenfunctions [5–9], application of the SO(2, 1) Lie algebra [10] and the use of hypervirial and Hellmann–Feynman theorems [11, 12]. When using parabolic coordinates one obtains the perturbation corrections to the separation constants and therefore one has to resort to the relation between them and the energy to obtain the perturbation corrections to the latter. To avoid this indirect procedure one can use spherical polar [13–16] or other coordinates [17] in which the Schrödinger equation is not separable. The main advantage of such approaches is that one can apply them to actually non-separable problems. The logarithmic derivative perturbation theory also applies under such conditions [15, 18]. In addition to it one can also use Lie algebraic methods [19–20], large-Z asymptotic expansions [13], polynomial expansions [17] or the celebrated F operator formalism [16] among other techniques. One can also obtain the perturbation corrections to the energy from the WKB method [21].

When one is mainly interested in large-order perturbation corrections to the energy a perturbation theory without wavefunction is advisable because it reduces the problem to the solution of relatively simple recurrence relations suitable for programming. One-dimensional and separable problems are most easily treated by means of the hypervirial perturbative method which yields the perturbation corrections as polynomial functions of the zeroth-order energy [11, 12]. In the case of non-separable problems one can use the moment method [22, 25]. Although in principle this approach applies to both non-degenerate and degenerate states no explicit calculation has been given for the latter [22-25].

The purpose of the present paper is to apply the moment method to degenerate states and disclose some properties of the formalism that have remained unnoticed. I outline the method in section 2 using spherical polar coordinates and derive equations that apply to all the states of the LoSurdo-Stark effect in hydrogen. In section 3 states that are not mixed by the perturbation are treated simultaneously and large-order results are shown for the ground state. In section 4 I illustrate the application of the method to degenerate states obtaining large-order perturbation corrections to the splitting of the second hydrogenic energy level. The last section is devoted to further comments and conclusions.

2. The method

The Hamiltonian operator for a hydrogen atom in a uniform static electric field can be written in atomic units (corrected to account for the reduced mass of the system) as

$$H = -\tfrac{1}{2}\Delta - \frac{1}{r} + \lambda z \tag{1}$$

where $r = (x^2 + y^2 + z^2)^{1/2}$ and λ is proportional to the strength of the electric field which is directed along the z axis. The moment method was presented in a quite general way elsewhere [25]; here I specialize in the problem above for the sake of concreteness. Furthermore, I arbitrarily choose spherical polar coordinates r, θ, and ϕ so that the perturbation is proportional to $z = r \cos \theta$. Straightforward application of H to the functions

$$F_{i,j,n,m} = \sin^i \theta \, \cos^j \theta \, r^n \, e^{-\beta r} \, e^{im\phi} \qquad i, j, \, n = 0, 1, \ldots, m = 0 \pm 1, \ldots \tag{2}$$

where $\beta > 0$, leads to

$$F_{i,j,n,m} = -\tfrac{1}{2}\beta^2 F_{i,j,n,m} + [\beta(n+1) - 1]F_{i,j,n-1,m} + \tfrac{1}{2}[(i+j)(i+j+1) - n(n+1)]F_{i,j,n-2,m}$$
$$+ \frac{m^2 - i^2}{2} F_{i-2,j,n-2,m} - \tfrac{1}{2}j(j-1)F_{i,j-2,n-2,m} + \lambda F_{i,j+1,n+1,m}. \tag{3}$$

Notice that the subscript i remains invariant if $i = |m|$ and that the coefficient of $F_{i,j,m-1,m}$ vanishes for $n = N - 1 = 0, 1, \ldots$ if $\beta = 1/N$. These choices greatly simplify the recurrence relation among the moments

$$I_{j,n} = \langle F_{|m|,j,n,m} | \Psi \rangle \tag{4}$$

in which Φ is an eigenfunction of H with eigenvalue E. I do not make explicit reference to m in the moments because this number does not change within the recurrence relation. Also notice that the functions $F_{i,j,n,m}$ as well as the eigenfunctions of H have definite parity with respect to the change of θ by $-\theta$.

It follows from $\langle (H-E)F_{i,j,n,m}|\Psi\rangle = 0$ that the moments (4) obey the recurrence relation

$$\frac{n+1-N}{N}I_{j,n-1}-\Delta E I_{n,n}+\tfrac{1}{2}[(|m|+j)(|m|+j+1)-n(n+1)]I_{j,n-2}$$

$$-\tfrac{1}{2}j(j-1)I_{j-2,n-2}+\lambda I_{j+1,n+1}=0 \tag{5}$$

where $\Delta E = E + 1/(2N^2)$. Substitution of the expansions

$$E = \sum_{q=0}^{\infty} E^{(q)} \qquad E^{(0)} = -1/(2N^2) \qquad I_{j,n} = \sum_{q=0}^{\infty} I_{j,n}^{(q)}\lambda^q \tag{6}$$

for E and the moments in (5) with n replaced by $n+1$ enables one to write

$$I_{j,n}^{(q)} = \frac{N}{n+2-N}\left\{\tfrac{1}{2}[(n+1)(n+2)-(|m|+j)(|m|+j+1)]I_{j,n-1}^{(q)}\right.$$

$$\left.+\tfrac{1}{2}j(j-1)I_{j-2,n-1}^{(q)}+\sum_{s=1}^{q}E^{(s)}I_{j,n+1}^{(q-s)}-I_{j+1,n+2}^{(q-1)}\right\}. \tag{7}$$

In order to obtain the perturbation corrections to the energy from this recurrence relation one needs an appropriate expression for E in terms of the moments (4). This expression which changes from state to state is derived for some particular cases in the following sections.

3. Non-mixing states

The choice $n = N-1 = |m|$ and $j=0$ leads to $\Delta E I_{0,N-1} = \lambda I_{1,N}$. Therefore, in terms of the new moments $A_{j,i} = I_{j,N-1+i}$, $i = 0, 1, \ldots$ equation (7) becomes

$$A_{j,i}^{(q)} = \frac{N}{i+1}\left\{\tfrac{1}{2}[(N+i)(N+i+1)-(j+N-1)(j+N)]A_{j,i-1}^{(q)}\right.$$

$$\left.+\tfrac{1}{2}j(j-1)A_{j-2,i-1}^{(q)}+\sum_{s=1}^{\infty}E^{(s)}A_{j,i+1}^{(q-s)}-A_{j+1,i+2}^{(q-1)}\right\} \tag{8}$$

and $\Delta E A_{0,0} = \lambda A_{1,1}$. Since the normalization of the wavefunction has no effect on the energy I choose $A_{0,0} = 1$ which provides both a simple starting point for the recurrence relation (8) and a simple expression for the perturbation corrections to the energy:

$$A_{0,0}^{(q)} = \delta_{q,0} \qquad q = 0, 1, \ldots \qquad E^{(q)} = A_{1,1}^{(q-1)} \qquad q = 1, 2, \ldots. \tag{9}$$

The calculation of the perturbation corrections to the energy by means of equations (8) and (9) is straightforward. Suffice to say that to obtain $E^{(p+1)}$ one needs $A_{j,i}^{(q)}$ $q = 0, 1, \ldots, p, j = 0, 1, \ldots, p-q+1$, and $i = 0, 1, \ldots, 2(p-q)+1$ from previous steps. These equations are suitable for both numerical and analytical calculations. In the latter case one can use standard computer algebra software and obtain many perturbation corrections exactly even with a personal computer.

The first four non-zero perturbation corrections to the energy for arbitrary values of N are shown in table 1 thus enlarging the result reported by Alliluev *et al* [8]. The calculation for particular values of N requires less memory space and can thereby be extended to larger orders. For instance, table 2 shows the first nine non-zero perturbation corrections to the energy of the ground state $(N = 1)$. This strategy for the calculation of the perturbation corrections to the energy of states that do not mix was successfully tried before for the Zeeman effect in hydrogen [25].

Table 1. First non-zero perturbation corrections to the energy of non-mixing states for arbitrary values of $|m| = N - 1 = 0, 1, \ldots$.

$E^{(2)} = N^4 \, (-5/8 - 9N/8 - N^2/2)$

$E^{(4)} = N^{10} \, (-55/8 - 1215N/64 - 2483N^2/128 - 1125N^3/128 - 3N^4/2)$

$E^{(6)} = N^{16}(-10\,625/32 - 290\,385N/256 - 409\,117N^2/256 - 615\,225N^3/512$
$\qquad = 524\,535N^4/1024 - 120\,789N^5/1024 - 23N^6/2)$

$E^{(8)} = N^{22}(-1078\,125/32 - 268\,318\,575N/2048 - 1809\,091\,955N^2/8192$
$\qquad - 3490\,153\,569N^3/16\,384 - 530\,817\,315N^4/4096 - 419\,370\,987N^5/8192$
$\qquad - 421\,808\,231N^6/32\,768 - 61\,889\,517N^7/32\,768 - 124N^8)$

Table 2. First non-zero perturbation corrections to the ground state energy $(|m| = N - 1 = 0)$.

p	$E^{(p)}$
2	$-9/2^2$
4	$-3\,555/2^6$
6	$-2\,512\,779/2^9$
8	$-13\,012\,777\,803/2^{14}$
10	$-25\,497\,693\,122\,265/2^{17}$
12	$-138\,963\,659\,571\,727\,791/2^{21}$
14	$-502\,057\,249\,081\,488\,605\,763/2^{24}$
16	$-18\,626\,167\,740\,853\,226\,792\,912\,715/2^{30}$
18	$-108\,153\,747\,299\,254\,161\,399\,143\,616\,141/2^{33}$

4. Degenerate states

The most attractive feature of the moment method is that most of its appealing simplicity remains when it is applied to degenerate states. Here I consider the splitting of the second unperturbed energy level. Of the four degenerate hydrogenic states 2s, $2p_0$ and $2p_{\pm 1}$ the last two ones have been considered in the previous section. For the sake of completeness table 3 shows the first nine non-zero perturbation corrections to the energy obtained from equations (8) and (9) with $N = 2$. The first six of them agree with those reported by Alliluev *et al* [6].

Table 3. First non-zero perturbation corrections to the energies of the $2p_{\pm 1}$ hydrogenic states $(|m| = N - 1 = 1)$.

p	$E^{(p)}$
2	-78
4	$-221\,952$
6	$-2\,052\,097\,536$
8	$-32\,263\,679\,717\,376$
10	$-720\,020\,129\,415\,168\,000$
12	$-21\,126\,901\,587\,942\,217\,089\,024$
14	$-783\,330\,762\,201\,061\,896\,077\,967\,360$
16	$-35\,828\,082\,494\,521\,876\,490\,094\,397\,882\,368$
18	$-1\,987\,499\,635\,795\,161\,159\,718\,505\,500\,177\,858\,560$

The states 2s and $2p_0$ mix when the field is turned on. To calculate the splitting I use the recurrence relations (5) and (7) with $m = 0$ and $N = 2$. When (j, n) in (5) is substituted for $(0, 0)$ and $(0, 1)$ one obtains two equations from which one can eliminate the undesired moment $I_{0,-1}$. The result is

$$\Delta E(I_{0,1} - 2I_{0,0}) = \lambda(I_{1,2} - 2I_{1,1}). \tag{10}$$

When $j = n = 1$ there is another useful relation between ΔE and the moments

$$\Delta E I_{1,1} = \lambda I_{2,2}. \tag{11}$$

An appropriate normalization condition is $I_{1,1} = 1$ because it leads to the simplest possible expression for the energy: $\Delta E = \lambda I_{2,2}$. Therefore,

$$I_{1,1}^{(q)} = \delta_{q,0} \qquad q = 0, 1, \ldots \tag{12}$$

and

$$E^{(q)} = I_{2,2}^{(q-1)} \qquad q = 1, 2, \ldots . \tag{13}$$

Furthermore, (10) reduces to

$$I_{2,2}(I_{0,1} - 2I_{0,0}) = I_{1,2} - 2. \tag{14}$$

When $\lambda = 0$ all the moments of the unperturbed states in this last equation can be expressed in terms of $I_{0,0}^{(0)}$ by means of the recurrence relation (7) (with $m = 0$ and $N = 2$). The resulting quadratic equation for this zeroth-order moment has two real roots

$$I_{0,0}^{(0)} = \pm \tfrac{1}{4} \tag{15}$$

because one is dealing with two states at the same time. Equations (12), (15) and the recurrence relation (7) determine the remaining zeroth-order moments. As a result one can obtain the first-order perturbation correction to the energy without calculating any integral form

$$E^{(1)} = I_{2,2}^{(0)} = \pm 3. \tag{16}$$

The calculation of the perturbation corrections of larger order requires an appropriate expression for $I_{0,0}^{(q)}$. One can obtain it by expansion of all the moments in (14) in λ-power series and reduction of $I_{0,1}^{(q)}$ and $I_{2,2}^{(q)}$ to $I_{0,0}^{(q)}$ by means of the recurrence relation (7). Then one can solve the resulting equation for the latter moment and reduce $I_{1,2}^{(q)}$ to corrections of smaller order using again the recurrence relation (7). The outcome of this straightforward procedure is

$$I_{0,0}^{(q)} = \frac{1}{24}\left\{ \sum_{s=1}^{q} E^{(s)}[\pm I_{1,3}^{(q-s)} - 6I_{2,2}^{(q-s)} - 8I_{0,2}^{(q-s)} - I_{2,3}^{(q-s)}] \pm \sum_{s=1}^{q-1} I_{2,2}^{(s)}[2I_{0,0}^{(q-s)} - I_{0,1}^{(q-s)}] \right.$$

$$\left. + 6I_{3,3}^{(q-1)} + 8I_{1,3}^{(q-1)} + I_{3,4}^{(q-1)} \mp I_{2,4}^{(q-1)} \right\} \tag{17}$$

where the $\pm$ and $\mp$ signs refer to the two states under consideration and come from the values of $I_{0,0}^{(0)}$ obtained above in (15). Now one can easily obtain all the perturbation corrections to the energy by means of equations (12), (13), (17) and the recurrence relation (7) with $N = 2$ and $m = 0$. To obtain $E^{(p+1)}$ one has to calculate $I_{j,n}^{(q)}$ with $q = 0, 1, \ldots p, j = 0, 1, \ldots, p - q + 2$, and $n = 1, 2, \ldots, 2(p - q) + 2$ in previous steps.

Table 4. Perturbation corrections to the energy splitting of the hydrogenic states 2s and $2p_0$ ($|m| = N - 2 = 0$).

p	$E^{(p)}$
1	± 3
2	-84
3	$\pm 1\,560$
4	$-257\,856$
5	$\pm 14\,214\,816$
6	$-2\,690\,869\,248$
7	$\pm 243\,073\,886\,976$
8	$-48\,538\,616\,082\,432$
9	$\pm 5\,925\,429\,002\,813\,952$
10	$-1\,247\,119\,322\,547\,093\,504$
11	$\pm 187\,912\,057\,677\,787\,975\,680$
12	$-41\,965\,106\,251\,721\,294\,217\,216$
13	$\pm 7\,428\,858\,655\,861\,394\,409\,406\,464$
14	$-1\,770\,053\,421\,993\,608\,758\,538\,797\,056$
15	$\pm 357\,540\,210\,738\,996\,369\,153\,435\,500\,544$
16	$-91\,188\,875\,752\,496\,789\,111\,151\,613\,968\,384$

Table 4 shows the first 16 perturbation corrections to the energy splitting of the states 2s and $2p_0$ which agree with a previous calculation [9].

5. Further comments and conclusions

I have shown that the moment method is suitable for the calculation of perturbation corrections to the energy and moments of the wavefunction for non-separable simple quantum mechanical systems. The technique applies to non-degenerate and degenerate states as well and seems to be much simpler than other approaches. The perturbation corrections are obtained from simple recurrence relations that are suitable for numerical as well as algebraic computation, the latter being facilitated by available software. It is worth noticing that all the information required to solve the problem is entirely contained in the recurrence relation. All the calculations reported here were carried out on a personal computer with an 8086 processor and the amount of data presented in the tables was limited by the 640 kb of computer memory space and the software used.

Here I have chosen the Stark effect in hydrogen as an illustrative example and benchmark. Because of its separability this problem has been treated by many authors and there are enough exact results available in the literature for one to test new approaches intensively. To my knowledge, a perturbation calculation of the order reported here has never been carried out in polar coordinates on the LoSurdo-Stark effect [15].

The moment method has been applied to the Zeeman effect in hydrogen which is non-separable [22-25]. However, only the unperturbed states that do not mix have been explicitly considered. The present treatment of the LoSurdo-Stark effect suggests that the remaining degenerate states of the Zeeman effect may offer no additional difficulty. The main difference between both problems is that in the latter the states of the first excited energy level of the hydrogen atom can be treated as if they were

non-degenerate because they do not mix. I am currently studying the Zeeman effect in hydrogen and will present results elsewhere in a forthcoming paper.

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