PHYSICAL REVIEW A VOLUME 46, NUMBER 1 1 JULY 1992

Perturbation theory without wave functions for the Zeeman effect in hydrogen

Francisco M. Fernandez* and Jorge A. Morales
Instituto de Investigaciones Fisicoquimicas Teoricas y Aplicadas (INIFTA), Division Quimica Teorica, Sucursal 4,
Casilla de Correo 16, 1900 La Plata, Argentina

(Received 21 October 1991; revised manuscript received 28 January 1992)

We apply perturbation theory to the hydrogen atom in a magnetic field by means of a recurrence relation for properly chosen moments of the wave function. The method is suitable for both numerical and symbolic computation and allows the treatment of classes of states with common symmetry properties. We derive analytic expressions in terms of the principal quantum number for the perturbation corrections to the energy of the unperturbed states with quantum numbers $n-1=|m|=l$, $n-2=|m|=l-1$, $n-2=|m|=l$, $n-3=|m|=l-1$, and $(n-3=|m|=l, n-3=|m|=l-2)$ some of which have not been reported before. Disagreements with some previous results are pointed out.

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

I. INTRODUCTION

Perturbation theory is one of the most widely used approximate methods in quantum mechanics. However, its application to nonseparable systems is commonly difficult, especially if one is interested in corrections of order greater than the second for degenerate states. Although the problem is nicely treated in most textbooks on quantum mechanics [1] the application of the perturbation formulas even to a system as simple as the Zeeman effect in hydrogen is far from trivial. This problem in particular has received considerable attention with regard to the study of large-order perturbation series and has for this reason become a benchmark for new perturbation techniques.

To apply perturbation theory one has to face at least two problems: the calculation of sufficient perturbation coefficients and the summation of the series that is typically divergent. Here we are concerned with the calculation of exact energy-perturbation coefficients. Such a calculation is only possible for simple systems such as the hydrogen atom with a multipole perturbation which is a tractable model for many physical phenomena. The Stark effect in hydrogen is separable in parabolic coordinates and for this reason the calculation of perturbation corrections is trivial [2]. The next simplest nonseparable problem of physical interest is the Zeeman effect in hydrogen. Roughly speaking there are two types of perturbation calculations on this system: low-order ones for many states and large-order ones for particular states. Typically, the former are directed to physical applications whereas the latter have mathematical goals. Since the standard perturbation formulas [1] are difficult to apply, many authors have proposed alternative techniques. Among the low-order calculations which are relevant to the present paper we mention straightforward integration of the perturbation differential equations in spherical coordinates [3] and the use of matrix methods for the Hamiltonian in spherical [4,5] or parabolic coordinates [6,7]. The most successful techniques for large-order calculations appear to be the Lie algebraic methods [8–14], the logarithmic-perturbation method [15–18], appropriate power-series expansion of the wave function [19,20], and the moment method [21–26].

The purpose of the present paper is threefold. First, we show that the moment method is a powerful tool for the exact calculation of perturbation correction to the energy of both nondegenerate and degenerate states. As an illustrative example we consider the Zeeman effect in hydrogen and point out some appealing features of the method unnoticed in previous applications [21–26]. Second, we show results that have not been reported before to our knowledge and that may be useful for physical applications of the model. Third, we compare the mutually disagreeing results of Galindo and Pascual [3], Chen [6], Grozdanov and Taylor [7], and Turbiner [16,17] with ours.

In Sec. II we outline the method and classify the states according to the master recurrence relation which we use to calculate the perturbation corrections. However, for the sake of clarity we also label the states with the hydrogenic quantum numbers n, l, and m which are adequate in the low-field regime. In Secs. III and IV we consider the states with $n-1=|m|=l$ and $n-2=|m|=l-1$, respectively, which have no radial nodes when the field vanishes. The former have been treated before by means of the moment method [24,25] but we include them here for the sake of completeness showing more exact energy coefficients. In Secs. V and VI we apply the method to the states with $n-2=|m|=l$ and $n-3=|m|=l-1$, respectively, each one with one radial node when there is no perturbation. The states we have mentioned so far can be treated by means of perturbation theory for nondegenerate states because the matrix elements of the perturbation between each one of them and any other state with the same energy vanish. In Sec. VII we consider the splitting of the pairs of states with $n-3=|m|=l-2$ and $n-3=|m|=l$. For all these cases we obtain the energy coefficients in terms of the principal quantum number n. In Sec. VIII we compare our results with those reported by other authors and in Sec. IX we discuss the advantages and limitations of the present approach as well as alternative ways of applying it.

II. THE METHOD

Only the part of the Hamiltonian operator for a hydrogen atom in a magnetic field that takes into account the diamagnetic effects is relevant to the present perturbation treatment. In atomic units it reads

$$H=H_0+\lambda H', \quad H_0=-\tfrac{1}{2}\Delta-\frac{1}{r}, \quad H'=x^2+y^2=r^2\sin^2\theta \ , \tag{1}$$

where $\lambda=B^2/8$, B being the strength of the field which is directed along the z axis. The main difficulty to overcome when treating this problem is that the unperturbed and perturbed parts of the Hamiltonian operator have different symmetries (spherical and cylindrical, respectively) and two degrees of freedom cannot be separated. The projection of the angular momentum onto the field direction is a constant of the motion related to the magnetic quantum number $m=0,\pm1,\ldots$ and the dependence of the wave function on the angle ϕ, which describes the motion of the system on the plane perpendicular to that direction, can be exactly factored out.

The moment method is based on the relation $\langle (H-E)F|\Psi\rangle=0$ in which Ψ is an eigenfunction of H with eigenvalue E and F is an element of a set of functions chosen so that HF can be written as a finite linear combination of functions of that set [24]. For the present problem we choose the functions

$$F_{i,j,n,m}(r,\theta,\phi)=\sin^i\theta\cos^j\theta\, r^n e^{-\beta r} e^{im\phi} \ , \tag{2}$$

where β is a positive constant to be determined and, $i,j,n=0,1,\ldots$. Straightforward application of H to (2) leads to

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

To simplify the moment recurrence relation we chose j to be either 0 or 1 and $\beta=1/N$, $N=1,2,\ldots$, so that $j(j-1)=0$ and $\beta(n+1)-1=0$ when $n=N-1$. Under such conditions we obtain the recurrence relation

$$\frac{n+1-N}{N}I_{i,n-1}-\Delta E I_{i,n}+\tfrac{1}{2}[(i+j)(i+j+1)-n(n+1)]I_{i,n-2}+\tfrac{1}{2}(m^2-i^2)I_{i-2,n-2}+\lambda I_{i+2,n+2}=0 \ , \tag{4}$$

for the moments $I_{i,n}=\langle F_{i,j,n,m}|\Psi\rangle$ in which we have defined $\Delta E=E+1/(2N^2)$. As far as the recurrence relation (4) is concerned j and N are constants of the motion, the former being related to the parity of the state Ψ and the latter being the hydrogenic principal quantum number. We find it convenient to classify the states with the values of $|m|$, j, and N although N is not a constant of the motion in the strict quantum-mechanical sense.

The parity of the functions (2) with respect to θ,

$$\begin{aligned} &F_{i,j,n,m}(r,-\theta,\phi)=(-1)^i F_{i,j,n,m}(r,\theta,\phi) \ , \\ &F_{i,j,n,m}(r,\theta+\pi,\phi)=(-1)^{i+j} F_{i,j,n,m}(r,\theta,\phi) \ , \end{aligned} \tag{5}$$

enables us to separate the states into four disjoint classes when $(i,i+j)$ is (even, even), (even, odd), (odd, even), or (odd, odd). As a result it is possible to treat the four unperturbed states with $n=2$ by means of nondegenerate perturbation theory because they belong to different classes. To label the Zeeman states by means of hydrogenic quantum numbers, notice that due to the parity of the spherical harmonics with respect to θ the unperturbed moments vanish unless $l-|m|=2k+j$, $k=0,1,\ldots$.

In order to apply perturbation theory we need an appropriate expression for ΔE in terms of the moments. We obtain it for the particular cases discussed in the following sections.

III. STATES WITH $j=0$ AND $|m|=N-1$

These states arise from hydrogenic ones with $N-1=l=|m|=0,1,\ldots$ and were treated before by means of the moment method [24,25]. When $i=n=N-1$ the recurrence relation (4) reduces to $\Delta E I_{N-1,N-1}=\lambda I_{N+1,N+1}$. Therefore, if we normalize the eigenfunction Ψ so that $I_{N-1,N-1}=1$, we obtain an expression for ΔE in terms of one of the moments: $\Delta E=\lambda I_{N+1,N+1}$. We can then use the recurrence relation (4) to express $I_{N+1,N+1}$ solely in terms of $I_{N-1,N-1}$ and other moments which, as they are multiplied by either ΔE or λ, contribute perturbation coefficients of lesser order. It follows from this fact that the moment recurrence relation, the normalization condition, and the expression for ΔE derived above are sufficient to obtain all the energy coefficients. Furthermore, since only one equation relating ΔE and the moments is sufficient to solve the problem we conclude that these states can be treated as nondegenerate.

The equations just discussed also appear in the standard Rayleigh-Schrödinger perturbation theory. If $\Psi^{(0)}$ is an eigenfunction of H_0 with eigenvalue $E^{(0)}=-1/(2N^2)$ then $\Delta E\langle\Psi^{(0)}|\Psi\rangle=\lambda\langle\Psi^{(0)}|H'|\Psi\rangle$. Therefore the normalization condition and the expression for the energy given above are equivalent to $\langle\Psi^{(0)}|\Psi\rangle=1$ and $\Delta E=\lambda\langle\Psi^{(0)}|H'|\Psi\rangle$, respectively. Because in the present case one can write $\Psi^{(0)}$ as a linear combination of the

TABLE I. Energy coefficients for the states with $j=0$ and $|m|=N-1$ $(N-1=|m|=l)$.

$$E_1=N^3(N+1)$$

$$E_2=N^7(N+1)(-7/3-9N/2-2N^2)$$

$$E_3=N^{11}(N+1)(88/3+850N/9+1024N^2/9+121N^3/2+12N^4)$$

$$E_4=N^{15}(N+1)(-858-35\,091N/10-362\,473N^2/60-607\,279N^3/108-322\,507N^4/108-6861N^5/8-104N^6)$$

$$\begin{aligned}E_5=N^{19}(N+1)(&134\,368/3+1\,899\,460N/9+296\,949\,121N^2/675+215\,854\,418N^3/405\\&+370\,883\,113N^4/900+22\,537\,787N^5/108+10\,957\,667N^6/162+102\,603N^7/8+1088N^8)\end{aligned}$$

$$\begin{aligned}E_6=N^{23}(N+1)(&-164\,270\,048/45-89\,448\,855\,628N/4725-210\,531\,466\,564N^2/4725\\&-17\,884\,076\,055\,179N^3/283\,500-33\,910\,358\,631\,211N^4/567\,000\\&-2\,420\,042\,788\,493N^5/60\,750-4\,601\,249\,807\,129N^6/243\,000-3\,087\,690\,077N^7/486\\&-2\,801\,202\,365N^8/1944-3\,190\,369N^9/16-12\,768N^{10})\end{aligned}$$

functions (2) we can express both equations in terms of the moments of Ψ.

To obtain general equations for all the states in the above mentioned class it is convenient to write $i=N-3+2s$ and $n=N-2+t$ where $s,t=1,2,\ldots$, and define $A_{s,t}=I_{i,n}$. In terms of these new moments the recurrence relation (4) reads

$$\begin{aligned}A_{s,t}=\frac{N}{t}\{&\tfrac{1}{2}[(N-1+t)(N+t)\\&-(N-3+2s)(N-2+2s)]A_{s,t-1}\\&+\tfrac{1}{2}[(N-3+2s)^2-(N-1)^2]A_{s-1,t-1}\\&+\Delta E A_{s,t+1}-\lambda A_{s+1,t+3}\}\ ,\end{aligned}\tag{6}$$

and the expression for the normalization condition and energy become $A_1=1$ and $\Delta E=\lambda A_{2,3}$, respectively.

We now apply perturbation theory by expanding ΔE and the moments in λ-power series

$$\Delta E=\sum_{p=1}^{\infty}E^{(p)}\lambda^p,\quad A_{s,t}=\sum_{p=0}^{\infty}A_{s,t}^{(p)}\lambda^p\ .\tag{7}$$

It follows from the recurrence relation (6) that the perturbation coefficients $E^{(p)}$ and $A^{(p)}$ are related by

$$\begin{aligned}A_{s,t}^{(p)}=\frac{N}{t}\Bigg\{&\frac{1}{2}[(N-1+t)(N+t)\\&-(N-3+2s)(N-2+2s)]A_{s,t-1}^{(p)}\\&+\tfrac{1}{2}[(N-3+2s)^2-(N-1)^2]A_{s-1,t-1}^{(p)}\\&+\sum_{j=1}^{p}E^{(j)}A_{s,t+1}^{(p-j)}-A_{s+1,t+3}^{(p-1)}\Bigg\}\ .\end{aligned}\tag{8}$$

The starting point of this recurrence relation comes from the normalization condition $A_1^{(p)}=\delta_{0p}$ and the perturbation corrections to the energy are given by $E^{(p)}=A_{2,3}^{(p-1)}$. According to the recurrence relation (8), to obtain $E^{(p+1)}=A_{2,3}^{(p)}$ we have to calculate $A_{s,t}^{(q)}$, $q=0,1,\ldots,p$, $s=1,2,\ldots,p-q+2$, $t=t_0,t_0+1,\ldots,3(p-q)+3$, where $t_0=2$ if $s=1$ and $t_0=2s-2$ otherwise.

By means of these equations we obtained the energy coefficients given in Table I as functions of N. These results enlarge those reported previously by Fernandez, Ogilvie, and Tipping [24] by one more perturbation correction.

IV. STATES WITH $|m|=N-2$ AND $j=1$

This class of states can also be labeled with the hydrogenic quantum numbers $N-2=|m|=l-1=0,1,\ldots$ and has not been treated before by means of the moment method [21–26]. Since the unperturbed states have no radial nodes and they can be treated as nondegenerate, the calculation procedure is similar to that in the preceding section. For this reason we show here only the final equations. In terms of the moments $A_{s,t}=I_{i,n}$, in which $i=N-4+2s$ and $n=N-2+t$, $s,t=1,2,\ldots$, we have

$$\begin{aligned}A_{s,t}=\frac{N}{t}\{&\tfrac{1}{2}[(N-1+t)(N+t)\\&-(N-3+2s)(N-2+2s)]A_{s,t-1}\\&+\tfrac{1}{2}[(N-4+2s)^2-(N-2)^2]A_{s-1,t-1}\\&+\Delta E A_{s,t+1}-\lambda A_{s+1,t+3}\}\ ,\end{aligned}\tag{9}$$

TABLE II. Energy coefficients for the states with $j=1$ and $|m|=N-2$ ($l=|m|+1$).

$$E_1=N^2(N^2-1)$$

$$E_2=-N^7(N^2-1)(2N+3)$$

$$E_3=N^{11}(N^2-1)(20/3+124N/3+42N^2+12N^3)$$

$$E_4=N^{15}(N^2-1)(-2182/15-19\,027N/30-49\,583N^2/36-24\,539N^3/18-2457N^4/4-104N^5)$$

$$\begin{aligned}E_5=N^{19}(N^2-1)(&83\,204/15+6\,225\,571N/225+16\,569\,383N^2/270+6\,157\,622N^3/75\\&+1\,232\,717N^4/18+926\,080N^5/27+9408N^6+1088N^7)\end{aligned}$$

$$\begin{aligned}E_6=N^{23}(N^2-1)(&-113\,120\,368/315-9\,112\,611\,974N/4725-111\,716\,048\,321N^2/23\,625\\&-1\,987\,894\,938\,829N^3/283\,500-189\,811\,488\,589N^4/27\,000-50\,083\,887\,413N^5/10\,125\\&-783\,044\,309N^6/324-252\,641\,845N^7/324-1\,192\,443N^8/8-12\,768N^9)\end{aligned}$$

together with the normalization condition $A_{1,1}=1$ and the energy expression $\Delta E=\lambda A_{2,3}$. From them one can easily derive a recurrence relation for the perturbation corrections $A_{s,t}^{(p)}$ and a formula for the energy coefficients which are almost identical to those in the preceding section.

Table II shows analytic expressions for the energy coefficients in terms of N.

V. STATES WITH $|m|=N-2$ AND $J=0$

This case corresponds to the hydrogenic quantum numbers $N-2=|m|=l=0,1,\ldots$. Only the 2s state has been treated before by means of the moment method [21,22,24,25]. To apply it to all the states in this class at the same time we define $A_{s,t}=I_{i,n}$, where $i=N-4+2s$ and $n=N-3+t$, $s,t=1,2,\ldots$. As a result the recurrence relation (4) becomes

$$\begin{aligned}\frac{t-1}{N}A_{s,t}=&\tfrac{1}{2}[(N-2+t)(N-1+t)-(N-4+2s)(N-3+2s)]A_{s,t-1}+\Delta E A_{s,t+1}\\&+\tfrac{1}{2}[(N-4+2s)^2-(N-2)^2]A_{s-1,t-1}-\lambda A_{s+1,t+3}\ .\end{aligned}\tag{10}$$

Notice that in this case we cannot make three terms vanish at the same time as we did in the two previous examples. The reason is that in the zero-field limit these states have one radial node. When (s,t) is replaced by (1,1) and (1,0) we have, respectively,

$$(N-1)A_{1,0}+\Delta E A_{1,2}-\lambda A_{2,4}=0\ ,\tag{11}$$

and

$$A_{1,0}=N(\lambda A_{2,3}-\Delta E A_{1,1})\ .\tag{12}$$

We eliminate $A_{1,0}$ from these two equations and obtain an expression for the energy: $\Delta E[A_{1,2}-N(N-1)A_{1,1}]=\lambda[A_{2,4}-N(N-1)A_{2,3}]$. To simplify it we choose the normalization condition

$$A_{1,2}-N(N-1)A_{1,1}=1\ ,\tag{13}$$

so that

$$\Delta E=\lambda[A_{2,4}-N(N-1)A_{2,3}]\ .\tag{14}$$

Equation (13) is insufficient to initiate the recursive process and we supplement it with another derived directly from (10) with $s=1$ and $t=2$,

$$A_{1,2}=N[(2N-1)A_{1,1}+\Delta E A_{1,3}-\lambda A_{2,5}]\ .\tag{15}$$

Substitution of this last equation into (13) gives us the starting point we are looking for,

$$A_{1,1}=N^{-2}(1-N\Delta E A_{1,3}+\lambda N A_{2,5})\ ,\tag{16}$$

which enables one to express $A_{1,1}^{(q)}$ in terms of $A_{1,3}^{(j)}$, $j<q$, and $A_{2,5}^{(q-1)}$ obtained in previous steps.

On expanding ΔE and every $A_{s,t}$ in λ-power series we obtain the set of equations

$$A_{1,1}^{(p)}=N^{-2}\left[\delta_{p0}-N\sum_{j=1}^{p}E^{(j)}A_{1,3}^{(p-j)}+NA_{2,5}^{(p-1)}\right]\ ,\tag{17a}$$

$$A_{s,t}^{(p)}=\frac{N}{t-1}\left\{\frac{1}{2}[(N-2+t)(N-1+t) -(N-4+2s)(N-3+2s)]A_{s,t-1}^{(p)} +\tfrac{1}{2}[(N-4+2s)^2-(N-2)^2]A_{s-1,t-1}^{(p)} +\sum_{j=1}^{p}E^{(j)}A_{s,t+1}^{(p-j)}-A_{s+1,t+3}^{(p-1)}\right\}, \tag{17b}$$

$$E^{(p)}=A_{2,4}^{(p-1)}-N(N-1)A_{2,3}^{(p-1)}, \tag{17c}$$

which allows the calculation of all the perturbation corrections. For every perturbation order one first uses (17a), then (17b) and finally (17c). In order to calculate $E^{(p+1)}$ we need $A_{s,t}^{(q)}$ with $q=0,1,\ldots,p$, $s=1,2,\ldots,p-q+2$, and $t=t_0,t_0+1,\ldots,3(p-q)+4$.

With the expressions above we have calculated the energy coefficients in terms of N given in Table III.

VI. STATES WITH $j=1$ AND $|m|=N-3$

In the zero-field limit these states become hydrogenic ones with $N-3=|m|=l-1$ which have one radial node. Since the treatment of such states parallels that in the preceding section we only show here the final results. The energy coefficients and perturbation corrections to the moments $A_{s,t}=I_{i,n}$, $i=N-5+2s$, $n=N-4+t$, $s,t=1,2,\ldots$, are given by

$$A_{1,2}^{(p)}=N^{-2}\left[\delta_{p0}-N\sum_{j=1}^{p}E^{(j)}A_{1,4}^{(p-j)}+NA_{2,6}^{(p-1)}\right], \tag{18a}$$

$$A_{s,t}^{(p)}=\frac{N}{t-2}\left\{\frac{1}{2}[(N-3+t)(N-2+t) -(N-4+2s)(N-3+2s)]A_{s,t-1}^{(p)} +\tfrac{1}{2}[(N-5+2s)^2-(N-3)^2]A_{s-1,t-1}^{(p)} +\sum_{j=1}^{p}E^{(j)}A_{s,t+1}^{(p-j)}-A_{s+1,t+3}^{(p-1)}\right\}, \tag{18b}$$

$$E^{(p)}=A_{2,5}^{(p-1)}-N(N-1)A_{2,4}^{(p-1)}. \tag{18c}$$

By means of these equations we obtained the energy coefficients in terms of N given in Table IV. This class of states was not treated before by means of the moment method.

VII. STATES WITH $j=0$ AND $|m|=N-3$

These states can be obtained by perturbation of the hydrogenic ones with $N-3=|m|=l$ and $N-3=|m|=l-2$ which mix when the field is turned on. This case illustrates the application of the moment method to perturbation theory for degenerate states. Such a calculation was not tried before although the applicability of the method to degenerate states was pointed out [21]. Strictly speaking all the unperturbed energy levels are degenerate when $N>1$. However, we treated the previous examples as nondegenerate states because we could separate them according to their symmetry. In the present case, on the other hand, the off-diagonal matrix elements of the perturbation between the states in each pair considered are nonzero and when using standard perturbation theory one is forced to obtain two linear combinations that make such matrix elements vanish. As shown below the moment method does not require the calculation of matrix elements and yields the energy splitting quite simply.

As before we shift the subscripts $i=N-5+2s$, $n=N-4+t$, and set $A_{s,t}=I_{i,n}$. To facilitate the discussion below we also define the quantities

$$\begin{aligned} a_{s,t}&=\tfrac{1}{2}[(N-5+2)(n-4+2s) -(n-4+t)(n-3+t)], \\ b_s&=\tfrac{1}{2}[(n-3)^2-(n-5+2s)^2], \end{aligned} \tag{19}$$

in terms of which the recurrence relation for the moments reads

TABLE III. Energy coefficients for the states with $j=0$ and $|m|=N-2$ $(l=|m|)$.

$$E_1=N^2(N-1)(N+5)$$

$$E_2=N^6(N-1)(-56+19N/3-25N^2-2N^3)$$

$$E_3=N^{10}(N-1)(1232-1652N/3+14\,596N^2/9+104N^3/9+260N^4+12N^5)$$

$$\begin{aligned} E_4=N^{14}(N-1)(&-33\,760+365\,698N/15-1\,615\,001N^2/18+26\,611N^3/20 \\ &-4\,849\,351N^4/108-339\,725N^5/108-13\,345N^6/4-104N^7) \end{aligned}$$

$$\begin{aligned} E_5=N^{18}(N-1)(&1\,034\,816-4\,482\,308N/5+1\,113\,064\,099N^2/225+774\,928\,777N^3/1350 \\ &+20\,437\,328\,903N^4/4050+594\,075\,014N^5/675+1\,190\,428N^6+17\,489\,737N^7/162 \\ &+94\,667N^8/2+1088N^9) \end{aligned}$$

TABLE IV. Energy coefficients for the states with $j=1$ and $|m|=N-3$ ($l=|m|+1$).

$$E_1=N^2(N-2)(5+N)$$

$$E_2=N^6(N-2)(-91+31N/2-47N^2/2-2N^3)$$

$$E_3=N^{10}(N-2)(3476-6356N/3+2062N^2-1835N^3/6+483N^4/2+12N^5)$$

$$\begin{aligned}E_4=N^{14}(N-2)(&-166\,344+2\,603\,299N/15-1\,076\,293N^2/6+3\,630\,613N^3/45\\&-586\,627N^4/12+253\,859N^5/72-24\,743N^6/8-104N^7)\end{aligned}$$

$$\begin{aligned}E_5=N^{18}(N-2)(&8\,919\,664-65\,902\,884N/5+3\,473\,510\,852N^2/225-7\,379\,400\,637N^3/675\\&+531\,353\,126N^4/75-2\,652\,120\,491N^5/1350+20\,414\,057N^6/18-5\,088\,821N^7/216\\&+351\,329N^8/8+1088N^9)\end{aligned}$$

$$\frac{t-3}{N}A_{s,t-1}+a_{s,t}A_{s,t-2}-\Delta E A_{s,t}+b_s A_{s-1,t-2}+\lambda A_{s+1,t+2}=0\ . \tag{20}$$

We substitute (1,3), (1,1), (2,3), and (1,2) for (s,t) and obtain

$$a_{1,3}A_{1,1}-\Delta E A_{1,3}+\lambda A_{2,5}=0\ , \tag{21}$$

$$-\frac{2}{N}A_{1,0}-\Delta E A_{1,1}+\lambda A_{2,3}=0\ , \tag{22}$$

$$-\Delta E A_{2,3}+b_2 A_{1,1}+\lambda A_{3,5}=0\ , \tag{23}$$

$$-\frac{1}{N}A_{1,1}+a_{1,2}A_{1,0}-\Delta E A_{1,2}+\lambda A_{2,4}=0\ , \tag{24}$$

respectively. Notice that except in the last case the choice of (s,t) was aimed to make two terms of (20) vanish. On eliminating $A_{1,0}$ between (22) and (24) we have

$$\Delta E(NA_{1,2}+\tfrac{1}{2}N^2a_{1,2}A_{1,1})-\lambda(NA_{2,4}+\tfrac{1}{2}N^2a_{1,2}A_{2,3})+A_{1,1}=0\ . \tag{25}$$

We obtain an appropriate expression for the energy by elimination of $A_{1,1}$ between (21) and (25):

$$\Delta E(Na_{1,3}A_{1,2}+\tfrac{1}{2}N^2a_{1,2}a_{1,3}A_{1,1}+A_{1,3})-\lambda(Na_{1,3}A_{2,4}+\tfrac{1}{2}N^2a_{1,2}a_{1,3}A_{2,3}+A_{2,5})=0\ . \tag{26}$$

The recurrence relation (20) and this last equation are insufficient to solve the problem as one can easily verify. Furthermore, if we eliminate $A_{1,1}$ between (21) and (23) we obtain another appropriate expression for the energy

$$\Delta E(a_{1,3}A_{2,3}-b_2A_{1,3})-\lambda(a_{1,3}A_{3,5}-b_2A_{2,5})=0\ . \tag{27}$$

The occurrence of two such equations is a direct consequence of twofold degeneracy. Inspection of the moment subscripts reveals that (25) and (27) correspond to unperturbed states with two radial nodes and one angular node, respectively. For $N=3$ they are the states $3s$ and $3d_0$, respectively, which have been treated by other methods [6,11,12]. Grozdanov and Taylor [7] obtained the first two energy coefficients for arbitrary values of N.

Equations (25) and (27) are linearly independent and we can obtain alternative pairs of equations by linear combination. The most convenient are those that lead to simpler expressions for the normalization condition and energy. As the former is arbitrary we simply select

$$a_{1,3}A_{2,3}-b_2A_{1,3}=1\ , \tag{28}$$

which leads to

$$\Delta E=\lambda(a_{1,3}A_{3,5}-b_2A_{2,5})\ . \tag{29}$$

If we substitute this last equation into (26) we obtain

$$(a_{1,3}A_{3,5}-b_2A_{2,5})(Na_{1,3}A_{1,2}+\tfrac{1}{2}N^2a_{1,2}a_{1,3}A_{1,1}+A_{1,3})-Na_{1,3}A_{2,4}-\tfrac{1}{2}N^2a_{1,2}a_{1,3}A_{2,3}-A_{2,5}=0\ . \tag{30}$$

Because the coefficient of $A_{s,2}$ vanishes for all s, the moment recurrence relation (20) does not allow the calculation of the perturbation corrections $A_{1,2}^{(p)}$ in terms of others of lesser order. However, by means of the equations above we can write the perturbation corrections to all the other moments in terms of $A_{1,2}^{(p)}$. To see this more clearly notice that we can start the calculation of the moment coefficients $A_{s,t}^{(p)}$ from $t=2s-2$ when $s>1$ because $a_{s,2s-1}=0$. We calculate the unknown perturbation coefficients $A_{1,2}^{(p)}$, $p=0,1,\ldots$ from the coefficients of the perturbation expansion of (30) which is quadratic in $A_{1,2}^{(0)}$ and linear in $A_{1,2}^{(p)}$ for all $p>0$. For $p=0$ we obtain two real roots that lead to the splitting of the energy levels. The derivation of the main equations is straightforward. We expand ΔE and the moments in λ-power series and obtain a recurrence relation for the coefficients from (20).

It gives us all the perturbation corrections in terms of $A_{1,2}^{(p)}$ except $A_{2,3}^{(p)}$ which one obtains from (28). From Eq. (30) we derive an equation for $A_{1,2}^{(p)}$ in terms of coefficients of lesser order. Finally, we obtain the energy coefficients from (29). We do not show the final expressions because they are similar to those used before. It is worth mentioning that if we had set the coefficient of ΔE in Eq. (26) equal to unity the unknown coefficient would have resulted to be $A_{2,2}^{(p)}$.

We have mentioned above that one can obtain an expression for $A_{1,2}^{(p)}$ in terms of coefficients of lesser order from Eq. (30). That expression turns out to be rather complicated and its derivation requires a good deal of careful algebraic manipulation. To avoid mistakes originating in this process we have opted for an alternative strategy. For every value of p we express all the perturbation coefficients in terms of $A_{1,2}^{(p)}$ and then solve the equation resulting from (3) by means of a symbolic processor. Table V shows some energy coefficients in terms of N.

VIII. COMPARISON WITH OTHER RESULTS

The noticeable disagreement between results obtained previously by other authors makes necessary a careful comparison with present calculations. To this end we

TABLE V. Energy coefficients for the states with $j=0$ and $|m|=N-3$ ($l=|m|$ and $l=|m|+2$).

$$R=\mp(41-48N+16N^2)^{1/2}$$

$$E_1=N^2(-7+3N+N^2+R)$$

$$D_2=82-260N+306N^2-160N^3+32N^4$$

$$\begin{aligned}E_2=N^6[&9758-39\,099N+66\,589N^2-64\,736N^3+40\,699N^4-17\,031N^5+4188N^6-304N^7-64N^8\\&+(-1578+5315N-7212N^2+5383N^3-2660N^4+912N^5-160N^6)R]/D_2\end{aligned}$$

$$\begin{aligned}D_3=&\,695\,137\,206-6\,849\,644\,664N+31\,331\,210\,916N^2-88\,237\,209\,624N^3+171\,042\,107\,766N^4\\&-241\,563\,402\,528N^5+256\,486\,982\,112N^6-208\,113\,850\,368N^7+129\,748\,442\,112N^8-61\,886\,742\,528N^9\\&+22\,242\,902\,016N^{10}-5\,844\,762\,624N^{11}+1\,062\,076\,416N^{12}-119\,537\,664N^{13}+6\,291\,456N^{14}\end{aligned}$$

$$\begin{aligned}E_3=N^{10}[&-2\,538\,641\,076\,312+27\,981\,284\,483\,332N-146\,344\,955\,934\,658N^2+483\,754\,819\,729\,749N^3\\&-1\,135\,433\,716\,783\,933N^4+2\,014\,654\,031\,158\,495N^5-2\,807\,950\,808\,664\,624N^6\\&+3\,151\,998\,895\,124\,191N^7-2\,897\,784\,879\,899\,977N^8+2\,206\,491\,846\,463\,521N^9\\&-1\,401\,621\,269\,720\,632N^{10}+745\,694\,106\,669\,136N^{11}-332\,428\,301\,729\,664N^{12}\\&+123\,634\,100\,038\,144N^{13}-37\,890\,996\,957\,184N^{14}+9\,327\,338\,692\,608N^{15}-1\,756\,261\,777\,408N^{16}\\&+229\,672\,026\,112N^{17}-16\,271\,278\,080N^{18}-66\,060\,288N^{19}+75\,497\,472N^{20}\\&+(391\,392\,434\,376-4\,088\,418\,968\,620N+20\,213\,301\,273\,002N^2-63\,007\,896\,329\,383N^3\\&\quad+139\,103\,353\,940\,024N^4-231\,472\,293\,993\,270N^5+301\,421\,107\,721\,846N^6\\&\quad-314\,547\,924\,622\,791N^7+267\,086\,360\,991\,880N^8-186\,318\,726\,785\,496N^9\\&\quad+107\,423\,331\,067\,648N^{10}-51\,366\,904\,787\,456N^{11}+20\,391\,291\,473\,152N^{12}\\&\quad-6\,697\,608\,839\,168N^{13}+1\,797\,313\,720\,320N^{14}-382\,236\,164\,096N^{15}\\&\quad+60\,559\,392\,768N^{16}-6\,325\,534\,720N^{17}+324\,009\,984N^{18})R]/D_3\end{aligned}$$

$$\begin{aligned}D_4=&\,70\,111\,538\,597\,160-995\,241\,840\,574\,320N+6\,708\,644\,050\,408\,920N^2\\&-28\,560\,955\,217\,289\,120N^3+86\,155\,354\,446\,799\,320N^4-195\,800\,908\,361\,151\,600N^5\\&+347\,956\,398\,768\,640\,680N^6-495\,263\,266\,529\,489\,280N^7+573\,592\,052\,157\,367\,680N^8\\&-546\,017\,813\,429\,575\,680N^9+429\,667\,775\,175\,444\,480N^{10}-280\,063\,956\,791\,623\,680N^{11}\end{aligned}$$

write $E_p(N,l,|m|)$ to indicate the pth energy coefficient in terms of the hydrogenic quantum numbers N, l, and m. Our results agree with independent calculations for the states $N=1$ and 2 [3,10,14,20] and with previous numerical and analytic applications of the moment method [21–25], one of which includes some states with $N=3$ and 4 [25].

Grozdanov and Taylor [7] calculated first- and second-order energy coefficients in terms of the principal quantum number N for many states and Turbiner [16,17] obtained the first three energy coefficients for a class of states with no radial nodes which corresponds to our classes ($j=0$, $|m|=N-1$) and ($j=1$, $|m|=N-2$). We agree with former authors except for the sign of their second-order coefficient. It appears that this sign should be reversed in view of the fact that their equations predict a positive second-order correction to the ground-state energy. Turbiner [16,17] points out that his results do not agree with Galindo and Pascual's [3] when $N=2$. We believe that Turbiner's expression does not hold for $N>1$. This author has not reported results for states having radial nodes probably because in such cases the logarithmic-perturbation equations become complicated as illustrated by the treatment of separable problems [27].

Chen [6] calculated first- and second-order energy coefficients for the states with $N=1$, 2, 3, and 4. Our re-

TABLE V. (*Continued*).

$$
\begin{aligned}
&+150\,985\,043\,808\,583\,680N^{12}-66\,974\,338\,677\,473\,280N^{13}+24\,212\,140\,319\,047\,680N^{14}\\
&-7\,025\,713\,584\,537\,600N^{15}+1\,598\,446\,444\,216\,320N^{16}-274\,883\,275\,653\,120N^{17}\\
&+33\,623\,554\,129\,920N^{18}-2\,609\,192\,632\,320N^{19}+96\,636\,764\,160N^{20}
\end{aligned}
$$

$$
\begin{aligned}
E_4=N^{14}[&7\,273\,090\,567\,914\,989\,760-115\,612\,391\,989\,027\,816\,656N+886\,326\,500\,722\,523\,977\,426N^2\\
&-4\,363\,646\,801\,622\,556\,655\,099N^3+15\,498\,112\,338\,949\,885\,068\,454N^4\\
&-42\,288\,735\,860\,993\,152\,863\,775N^5+92\,199\,583\,256\,211\,448\,575\,173N^6\\
&-164\,960\,482\,628\,758\,460\,105\,668N^7+246\,927\,218\,642\,426\,854\,716\,987N^8\\
&-313\,824\,254\,644\,782\,741\,376\,482N^9+342\,611\,513\,201\,057\,326\,625\,145N^{10}\\
&-324\,374\,802\,415\,794\,942\,395\,325N^{11}+268\,409\,874\,780\,399\,717\,902\,895N^{12}\\
&-195\,303\,227\,335\,635\,663\,078\,915N^{13}+125\,498\,732\,802\,509\,183\,845\,440N^{14}\\
&-71\,374\,604\,575\,588\,545\,969\,360N^{15}+35\,925\,116\,997\,120\,376\,211\,712N^{16}\\
&-15\,966\,480\,668\,647\,985\,962\,752N^{17}+6\,238\,826\,531\,803\,683\,790\,848N^{18}\\
&-2\,130\,119\,760\,575\,590\,699\,008N^{19}+630\,291\,555\,203\,104\,440\,320N^{20}\\
&-159\,794\,027\,617\,615\,151\,104N^{21}+34\,116\,720\,049\,032\,003\,584N^{22}-5\,963\,598\,337\,242\,300\,416N^{23}\\
&+812\,650\,512\,951\,279\,616N^{24}-78\,622\,902\,336\,880\,640N^{25}+4\,283\,191\,032\,545\,280N^{26}\\
&-7\,428\,951\,244\,800N^{27}-10\,050\,223\,472\,640N^{28}\\
&+(-1\,143\,759\,859\,158\,588\,480+17\,503\,591\,071\,388\,588\,224N-128\,971\,450\,686\,128\,970\,778N^2\\
&\quad+609\,180\,898\,850\,145\,956\,459N^3-2\,071\,739\,328\,168\,767\,153\,410N^4\\
&\quad+5\,401\,937\,671\,025\,627\,485\,375N^5-11\,230\,359\,489\,094\,326\,021\,212N^6\\
&\quad+19\,118\,286\,423\,272\,566\,227\,259N^7-27\,173\,405\,800\,695\,041\,575\,242N^8\\
&\quad+32\,730\,756\,954\,254\,345\,208\,465N^9-33\,812\,643\,322\,702\,804\,768\,110N^{10}\\
&\quad+30\,253\,071\,558\,796\,922\,243\,850N^{11}-23\,629\,562\,874\,700\,296\,870\,960N^{12}\\
&\quad+16\,206\,000\,408\,799\,367\,954\,400N^{13}-9\,793\,171\,017\,629\,093\,406\,720N^{14}\\
&\quad+5\,218\,150\,158\,177\,142\,863\,360N^{15}-2\,446\,835\,501\,043\,342\,809\,088N^{16}\\
&\quad+1\,005\,436\,886\,701\,371\,580\,416N^{17}-359\,958\,924\,092\,651\,225\,088N^{18}\\
&\quad+111\,517\,718\,743\,911\,628\,800N^{19}-29\,657\,205\,381\,398\,528\,000N^{20}\\
&\quad+6\,695\,132\,027\,636\,678\,656N^{21}-1\,259\,142\,241\,385\,971\,712N^{22}+190\,607\,352\,645\,287\,936N^{23}\\
&\quad-21\,794\,916\,904\,468\,480N^{24}+1\,665\,386\,990\,796\,800N^{25}-63\,248\,762\,142\,720N^{26})R]/D_4
\end{aligned}
$$

sults disagree with Chen's [6] for $E_2(4,3,3)$, $E_2(3,1,1)$, $E_1(4,2,2)$, $E_2(4,2,2)$, $E_2(3,2,1)$, and $E_2(4,3,2)$. Moreover, our results for the splitting of the states with $j=0$ and $|m|=N-3$ are in complete agreement with the large-order numerical calculation of Silverstone and Moats [12] for $N=3$ but share no resemblance at all with the energy coefficients reported by Chen [6].

IX. FURTHER COMMENTS AND CONCLUSIONS

We have shown that the moment method greatly facilitates the application of perturbation theory to simple nonseparable quantum-mechanical systems. It allows the treatment of both nondegenerate and degenerate states and is suitable for numerical as well as analytic calculation using computer algebra. The method bypasses the calculation of matrix elements and integrals required by other approaches and its efficiency can be seen in that we have carried out our calculations on a 640-kbyte personal computer and have obtained analytic and exact rational energy coefficients (not shown here) of much larger order than those reported by other authors. Only the results in Table V required the use of a more powerful computer. Many of the energy coefficients shown in Tables I–V were not reported before and they may be useful in physical applications. Here we have used them to decide which of the mutually disagreeing results reported by other authors require modification.

Another practical advantage of the moment method is that when the perturbation series is divergent, as in the present case, one can easily introduce an adjustable parameter into the recurrence relation to obtain renormalized series with improved convergence properties [26] (alternative approaches are discussed in Ref. [25]). In our opinion the moment method is much simpler than other implementations of perturbation theory such as the Lie algebraic method [8–14] or the logarithmic-perturbation method [15–17]. However, the latter two procedures are preferable when one is interested in the calculation of physical properties other than the energy which require explicit use of the eigenfunction. In particular the powerful Lie algebraic method is suitable for the calculation of matrix elements of operators that can be written in terms of the generators of the algebra [8,14]. However, in any case the moment method may be useful to verify the results obtained by means of those other techniques.

We have pointed out that the general equations for the degenerate states treated above are complicated. This fact may be traceable to the coordinate system that is being used. It must be kept in mind that one can apply the moment method with any convenient coordinate system and that the equations may be much simpler in one system than in another. For instance, in the case of the Zeeman effect in hydrogen one can as well use cylindrical or parabolic coordinates. We are presently investigating such alternatives and the application of the moment method to other physical systems.

ACKNOWLEDGMENT

We would like to thank Dr. J. F. Ogilvie for having sent us two procedures written in the computer environment REDUCE that we required to obtain the results in Table V.

---

*Present address: Programa QUINOR, Facultad de Ciencias Exactas, Universidad Nacional de la Plata, Calle 47 y 115, Casilla de Correo 962, 1900 La Plata, Argentina.

[1] A. Messiah, *Mécanique Quantique* (Dunod, Paris, 1964), Vol. II, Chap. XVI.
[2] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), Chap. III.
[3] A. Galindo and P. Pascual, Nuovo Cimento B **34**, 155 (1976).
[4] H. Ruder, G. Wunner, H. Herold, and M. Reinecke, J. Phys. B **14**, L45 (1985).
[5] G. Wunnder, J. Phys. B **19**, 1623 (1986).
[6] A. C. Chen, Phys. Rev. A **28**, 280 (1983); **29**, 2225 (1984).
[7] T. P. Grozdanov and H. S. Taylor, J. Phys. B **19**, 4075 (1986).
[8] M. Bednař, Ann. Phys. (N.Y.) **75**, 305 (1973).
[9] M. Bednař, Phys. Rev. A **15**, 27 (1977).
[10] J. E. Avron, B. G. Adams, J. Čižek, M. Clay, M. L. Glasser, P. Otto, J. Paldus, and E. Vrscay, Phys. Rev. Lett. **43**, 691 (1979).
[11] B. G. Adams, J. E. Avron, J. Čižek, P. Otto, J. Paldus, R. K. Moats, and H. J. Silverstone, Phys. Rev. A **21**, 1914 (1980).
[12] H. J. Silverstone and R. K. Moats, Phys. Rev. A **23**, 1645 (1981).
[13] J. Čižek and E. R. Vrscay, Int. J. Quantum Chem. **21**, 27 (1982).
[14] B. G. Adams, J. Čižek, and J. Paldus, Adv. Quantum Chem. **19**, 1 (1988).
[15] A. V. Turbiner, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 165 (1981) [JEPT Lett. **33**, 173 (1981)].
[16] A. V. Turbiner, Z. Phys. A **308**, 111 (1981).
[17] A. V. Turbiner, J. Phys. A **17**, 859 (1984).
[18] J. C. Le Guillou and J. Zinn-Justin, Ann. Phys. (N.Y.) **147**, 57 (1983).
[19] B. R. Johnson, K. F. Scheibner, and D. Farrelly, Phys. Rev. Lett. **51**, 2280 (1983).
[20] W. Janke, Phys. Rev. A **41**, 6071 (1990).
[21] F. M. Fernandez and E. A. Castro, Int. J. Quantum Chem. **26**, 497 (1984).
[22] G. A. Arteca, F. M. Fernandez, A. M. Meson, and E. A. Castro, Physica A **128**, 253 (1984).
[23] F. M. Fernandez and E. A. Castro, Int. J. Quantum Chem. **28**, 603 (1985).
[24] F. M. Fernandez, J. F. Ogilvie, and R. H. Tipping, J. Phys. A **20**, 3777 (1987).
[25] G. A. Arteca, F. M. Fernandez, and E. A. Castro, in *Large Order Perturbation Theory and Summation Methods in Quantum Mechanics,* Lecture Notes in Chemistry Vol. 53 (Springer-Verlag, Berlin, 1990).
[26] E. J. Austin, Int. J. Quantum Chem. **18S**, 449 (1984).
[27] S. P. Alliluev, V. L. Eletsky, V. S. Popov, and V. M. Weinberg, Phys. Lett. **78A**, 43 (1980).