Perturbation theory from moment recurrence relations

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Abstract. Moment recurrence relations are shown to be useful in perturbation calculations. General equations are developed and different cases are discussed. The anharmonic oscillator and Zeeman effect in hydrogen are used as illustrative examples.

1. Introduction

Perturbation theory approaches that do not take into account the eigenfunctions explicitly prove to be very useful in calculating large-order Rayleigh-Schrödinger coefficients for the eigenvalues. The first method developed by Swenson and Danforth (1972) was based on the virial and Hellmann-Feynman theorems and was successfully applied to a large number of quantum mechanical models (Fernández and Castro 1984a and references therein). A quite general formulation of the procedure was given by Fernández and Castro (1984a) who discussed the conditions under which the method can be applied. With a slight modification the hypervirial perturbative method is particularly useful in dealing with quantum mechanical models with finite boundary conditions (Fernández and Castro 1982 and references therein). As far as we know, no other procedure has been successfully applied to such systems.

Unfortunately, the hypervirial perturbative method cannot be applied to non-separable multidimensional problems. However, Fernández and Castro (1984b, 1985) have recently developed a perturbation theory without wavefunction for such systems. The method based on moment recurrence relations was first applied to the hydrogen atom in magnetic and electric fields (Fernández and Castro 1984b, 1985, Arteca *et al* 1984, Austin 1984) and its application to coupled oscillators was suggested (Fernández and Castro 1985). The importance of the moment recurrence relations had been previously noticed by Blankenbecler *et al* (1980) who performed non-perturbative eigenvalue calculations.

A perturbational approach for one- and two-dimensional anharmonic oscillators was recently reported by Killingbeck *et al* (1985) and Killingbeck and Jones (1986). In the latter case the authors managed to deal with degenerate states by taking into account explicitly the appropriate symmetry of the eigenfunctions.

Although the wide applicability of the moment method has been suggested (Fernández and Castro 1984b) we find that there is a lack of a general formulation showing its possibilities and limitations. The aim of the present paper is to develop the moment perturbation theory (MPT) in a more general way. The main equations are given in

§ 2 where two different cases are discussed and illustrated by means of the anharmonic oscillator. It is shown in § 3 that under certain conditions the moment recurrence relation becomes the secular equation leading to a most convenient perturbation approach. The Zeeman effect in hydrogen is discussed in § 4 and results for some states are shown in §§ 5 and 6. Further comments and conclusions are found in § 7.

2. The moment method

The moments of a function Ψ are defined as (Epstein 1974) $\langle F|\Psi\rangle$ where F is any function such that the inner product exists. We are interested in the moments of the eigenfunctions of the time-independent Schrödinger equation

$$H\Psi = E\Psi. \tag{2.1}$$

Clearly,

$$\langle\Psi|H|F\rangle = E\langle\Psi|F\rangle \tag{2.2}$$

for any function F belonging to the domain of the Hamiltonian operator H.

We further assume that H can be written as $H = H_0 + \lambda V$, where the eigenvalues and eigenfunctions of H_0 are available:

$$H_0\Phi_i = E_i^{(0)}\Phi_i. \tag{2.3}$$

Therefore, a set of functions $\{F_i\}$ ($i = 1, 2, \ldots$) exists so that

$$H_0F_i = \sum_{j=1}^{i} h_{j,i}F_j. \tag{2.4}$$

If in addition to this it is found that

$$VF_i = \sum_{j=i-I}^{i+I'} v_{j,i}F_j \tag{2.5}$$

where $I, I' > 0$, then equation (2.2) with $F = F_i$ leads to

$$\sum_{j=1}^{i} h_{j,i}A_j + \lambda \sum_{j=i-I}^{i+I'} v_{j,i}A_j - EA_i = 0 \tag{2.6}$$

where $A_j = \langle\Psi|F_j\rangle$.

If E and the moments A_j are expanded in powers of λ:

$$E = \sum_{q=0}^{\infty} E^{(q)}\lambda^q \qquad A_j = \sum_{q=0}^{\infty} A_j^{(q)}\lambda^q \tag{2.7}$$

then equation (2.6) becomes a recurrence relation for the perturbation corrections. All of them can be calculated provided certain conditions are fulfilled.

The starting point or initial condition is obtained as follows. According to equation (2.4) a linear combination

$$\Phi = \sum_{j=1}^{m} C_jF_j \tag{2.8}$$

can be chosen to be an eigenfunction of H_0:

$$H_0\Phi = E^{(0)}\Phi. \tag{2.9}$$

Therefore, equation (2.2) with $F = \Phi$ yields

$$\varepsilon \langle \Psi | \Phi \rangle = \lambda \langle \Psi | V | \Phi \rangle \tag{2.10}$$

where $\varepsilon = E - E^{(0)}$.

If the functions F_j are linearly independent, it follows from (2.4), (2.8) and (2.9) that $h_{m,m} = E^{(0)}$ and

$$C_k = (E^{(0)} - h_{k,k})^{-1} \sum_{j=k+1}^{m} C_j h_{k,j} \qquad k < m. \tag{2.11}$$

Therefore, all the coefficients C_k can be obtained in terms of C_m which can be arbitrarily chosen. Equation (2.6) can then be written

$$\sum_{j=1}^{i-1} h_{j,i} A_j + \lambda \sum_{j=i-1}^{i+1'} v_{j,i} A_j - \varepsilon A_i = (h_{m,m} - h_{i,i}) A_i \tag{2.12}$$

which is our main equation.

If $h_{m,m} \neq h_{i,i}$ when $m \neq i$ we choose $A_m = 1$ in equation (2.12) and introduce the expansion (2.7). The result is

$$E^{(p)} = \sum_{j=1}^{m-1} h_{j,m} A_j^{(p)} + \sum_{j=m-1}^{m+1'} v_{j,m} A_j^{(p-1)} \qquad p > 0 \tag{2.13a}$$

$$A_i^{(p)} = (h_{m,m} - h_{i,i})^{-1} \left(\sum_{j=1}^{i-1} h_{j,i} A_j^{(p)} - \sum_{q=1}^{p} E^{(q)} A_i^{(p-q)} \right.$$
$$\left. + \sum_{j=i-1}^{i+1'} v_{j,i} A_j^{(p-1)} \right) \qquad m \neq i, p \geq 0 \tag{2.13b}$$

from which all the perturbation corrections can be obtained because $A_m^{(p)} = \delta_{p,0}$. We can derive a sole equation for the corrections $A_i^{(p)}$ by introducing (2.13a) into (2.13b). This calculation scheme is possible in the case of anharmonic oscillators as shown by Killingbeck *et al* (1985) and Killingbeck and Jones (1986).

When the functions F_j are of hydrogenic type, as in the case of the Zeeman and Stark effect in hydrogen, it is found that $h_{i,i} = h_{m,m}$ for all i and, therefore, we have to proceed in a different way (Fernández and Castro 1984b, 1985). First of all we rewrite equation (2.13b) as

$$h_{i-1,i} A_{i-1}^{(p)} = - \sum_{j=1}^{i-2} h_{j,i} A_j^{(p)} + \sum_{q=1}^{p} E^{(q)} A_i^{(p-q)} - \sum_{j=i-1}^{i+1'} v_{j,i} A_j^{(p-1)}. \tag{2.14a}$$

Also, the normalisation condition $A_m = 1$ proves to be useless in this case and one has to resort to the standard one, namely $\langle \Psi | \Phi \rangle = 1$ which, together with equation (2.10), leads to

$$\sum_{j=1}^{m} C_j A_j^{(p)} = \delta_{p,0} \tag{2.14b}$$

$$E^{(p)} = \sum_{i=1}^{m} \sum_{j=i-1}^{i+1'} C_i v_{j,i} A_j^{(p-1)}. \tag{2.14c}$$

It is straightforward to verify that equation (2.14a) with $i = 2, 3, \ldots, m+1$ and equation (2.14b) enable one to calculate $A_j^{(p)}$, $j = 1, 2, \ldots, m$, in terms of perturbation corrections of order smaller than p. Therefore, all the perturbation corrections can be obtained from equations (2.14).

In order to exemplify the difference between the two procedures just outlined let us consider the very simple problem posed by the anharmonic oscillator:

$$H = H_0 + \lambda x^{2\nu} \qquad \nu = 2, 3, \ldots \tag{2.15}$$

where $H_0 = -\mathrm{d}^2/\mathrm{d}x^2 + x^2$. The choice of $F_N = x^N \exp(-x^2/2)$ leads to

$$(2N + 1 - E)A_N - N(N-1)A_{N-2} + \lambda A_{N+2\nu} = 0 \tag{2.16}$$

where $N = 0, 2, \ldots$, or $N = 1, 3, \ldots$, for the even or odd states, respectively. A straight-forward algebraic manipulation shows that (cf equations (2.13))

$$E^{(p)} = -m(m-1)A_{m-2}^{(p)} + A_{m+2\nu}^{(p-1)} \qquad p > 0 \tag{2.17a}$$

$$A_N^{(p)} = \frac{1}{2(N-m)} \left(N(N-1)A_{N-2}^{(p)} + \sum_{q=1}^{p} E^{(q)}A_N^{(p-q)} - A_{N+2\nu}^{(p-1)} \right) \qquad N \neq m, p \geq 0 \tag{2.17b}$$

where $E^{(0)} = 2m + 1$ and $A_m^{(p)} = \delta_{p,0}$.

When $m = 0$ or 1 both procedures lead to the same equations and to show the difference between them we discuss the second excited state $m = 2$. On substituting $N = 0$ and $N = 2$ in (2.16) and rearranging the resulting equations, one easily finds (cf equation (2.10)) $(E - 5)(A_0 - 2A_2) = \lambda(A_2 - 2A_{2\nu+2})$ which enables one to choose $2A_2 - A_0 = 1$ (normalisation condition). These equations can be rewritten

$$E = 5 + \lambda(A_2 - 2A_{2\nu+2}) \tag{2.18a}$$

$$A_0 = \tfrac{1}{2}\lambda[A_2(A_{2\nu} - 2A_{2\nu+2}) + A_{2\nu+2}] \tag{2.18b}$$

$$A_2 = \tfrac{1}{2} + \tfrac{1}{2}A_0 \tag{2.18c}$$

from which one can obtain $E^{(p)}$, $A_0^{(p)}$ and $A_2^{(p)}$ in terms of perturbation corrections of order smaller than p. Finally, if we write $E = 5 + \varepsilon$ in equation (2.16) and make use of equation (2.18a), we obtain

$$A_N = \frac{1}{2(N-2)}[N(N-1)A_{N-2} - \lambda A_{N+2} + \lambda A_N(A_{2\nu+2} - A_{2\nu})] \qquad N = 4, 6, \ldots \tag{2.18d}$$

which enables one to calculate the remaining $A_N^{(p)}$.

In the example given above the first procedure is more convenient because the form of the equations is the same for all the states. The second procedure, on the other hand, requires that each state be treated separately because it is necessary to solve the above-mentioned set of m equations for $A_j^{(p)}$ ($j \leq m$) before proceeding further. Unfortunately, in some cases $h_{m,m} = h_{i,i}$ and one is forced to use the second procedure, as shown in §§ 4 and 5.

We deem it necessary to add that in obtaining the general equations above we have assumed that there is only one state Φ with energy $E^{(0)}$. Degenerate states can also be treated, as discussed by Fernández and Castro (1984b) and Killingbeck and Jones (1986).

3. The secular equation

As shown in the previous section the eigenfunctions of H_0 play a relevant role in obtaining the proper moment recurrence relation. This fact suggests that it may be

advantageous to use the recurrence relation for the moments $A_{j,n} = \langle \Psi_n | \Phi_j \rangle$, $j = 1, 2, \ldots$ (where Ψ_n is a given eigenfunction of H with eigenvalue E_n). Obviously, when doing this we are led to the secular equation

$$\varepsilon_{n,i} A_{i,n} = \lambda \sum_j V_{j,i} A_{j,n} \tag{3.1}$$

where $\varepsilon_{n,i} = E_n - E_i^{(0)}$ and $V_{j,i} = \langle \Phi_j | V | \Phi_i \rangle$. For the sake of simplicity the set of eigenfunctions of H_0 is assumed to be orthonormal, in which case the moments become the expansion coefficients of Ψ_n in terms of the basis $\{\Phi_i\}$.

If we are interested in the perturbed energy levels that tend to $E_n^{(0)}$ as $\lambda \to 0$, then it is advisable to set $A_{n,n} = 1$. Therefore equation (3.1) with $i = n$ gives us the following expression for the energy:

$$E_n = E_n^{(0)} + \lambda \sum_j V_{j,n} A_{j,n}. \tag{3.2}$$

This last equation enables us to rewrite (3.1) (for $i \neq n$) as

$$\omega_{n,i} A_{i,n} = \lambda \left(\sum_j V_{j,i} A_{j,n} - A_{i,n} \sum_j V_{j,n} A_{j,n} \right) \qquad i \neq n \tag{3.3}$$

where $\omega_{n,i} = E_n^{(0)} - E_i^{(0)}$. Finally, the perturbation corrections for the energy and moments are found to obey

$$E_n^{(p)} = \sum_j V_{j,n} A_{j,n}^{(p-1)} \qquad p > 0 \tag{3.4a}$$

$$\omega_{n,i} A_{i,n}^{(p)} = \sum_j V_{j,i} A_{j,n}^{(p-1)} - \sum_{q=0}^{p-1} A_{i,n}^{(p-q-1)} \sum_j V_{j,n} A_{j,n}^{(q)} \qquad i \neq n \tag{3.4b}$$

where

$$A_{i,n}^{(0)} = \delta_{i,n} \qquad A_{n,n}^{(p)} = \delta_{p,0}. \tag{3.4c}$$

When $V_{i,j} = 0$, for all $|i - j| > J$ the perturbation corrections can be exactly calculated by means of equations (3.4). However, a careful choice of the zeroth-order eigenfunctions is required when $E_n^{(0)}$ is degenerate. For instance, suppose that $E_i^{(0)} = E^{(0)}$ for all i belonging to a set I_0 of integer numbers. Then it follows immediately from (3.4) with $p = 1$ that

$$V_{n,i} = E_n^{(1)} \delta_{n,i} \qquad i, n \in I_0. \tag{3.5}$$

In other words, from all the linear combinations of eigenfunctions of H_0 corresponding to $E^{(0)}$ we have to select those yielding a diagonal V matrix. This is a well known result in perturbation theory.

The states with non-degenerate first-order corrections can be treated in a straightforward manner through equations (3.4). However, if $E_i^{(1)} = E^{(1)}$ for all $i \in I_1 \subseteq I_0$, then equations (3.4) lead to another well known expression:

$$\sum_{j \notin I_0} \omega_{n,j}^{-1} V_{i,j} V_{j,n} = E_n^{(2)} \delta_{n,i} \qquad n, j \in I_1. \tag{3.6}$$

Higher-order perturbation corrections can be obtained in the same way.

A more general and convenient formulation of the secular equation approach is obtained by using an arbitrary orthonormal basis set $\{|i\rangle\}$. On setting $A_{n,n} = 1$ the equation for the moments (or expansion coefficients) $A_{j,n} = \langle \Psi_n | j \rangle$ is found to be

$$E_n = H_{n,n} + \sum_{j \neq n} H_{j,n} A_{j,n} \tag{3.7}$$

$$(H_{n,n} - H_{i,i}) A_{i,n} = \sum_{j \neq i} H_{j,i} A_{j,n} - A_{i,n} \sum_{j \neq n} H_{j,n} A_{j,n} \tag{3.8}$$

where $H_{i,j} = \langle i|H|j \rangle$. If the non-diagonal part of H is treated as a perturbation, the following recurrence relation for the moment perturbation corrections is obtained:

$$(H_{n,n} - H_{i,i})A_{i,n}^{(p)} = \sum_{j \neq i} H_{j,i}A_{j,n}^{(p-1)} - \sum_{q=0}^{p-1} A_{i,n}^{(p-q-1)} \sum_{j \neq n} H_{j,n}A_{j,n}^{(q)} \qquad (3.9a)$$

$$E_n^{(p)} = H_{n,n}\delta_{p,0} + \sum_{j \neq n} H_{j,n}A_{j,n}^{(p-1)} \qquad (3.9b)$$

$$A_{j,n}^{(0)} = \delta_{j,n} \qquad A_{n,n}^{(p)} = \delta_{p,0}. \qquad (3.9c)$$

These equations are handled as shown before and when $H_{i,j} = 0$ for all $|i - j| > J$ they yield the perturbation corrections exactly.

This method proves to be very powerful in dealing with one- and two-dimensional anharmonic oscillators (Fernández et al 1984b, 1985b) and central-field models (Fernández et al 1985a). In most of the perturbation approaches (see, for example, Fernández et al 1984a, Killingbeck and Jones 1986 and references therein) the Hamiltonian operator is split in such a way that part of H_0 is added to the perturbation. In the present case, on the other hand, the diagonal part of the perturbation is contained in the unperturbed operator. For this reason the method just sketched seems to be preferable in dealing with strongly singular perturbations like that in the anharmonic oscillator.

4. The Zeeman effect in hydrogen

The general procedures developed in the previous sections are useful in dealing with multidimensional problems. For example, the quantum mechanical model

$$H_0 = -\tfrac{1}{2}\Delta - 1/r \qquad V = \tfrac{1}{8}r^2 \sin^2 \theta \qquad (4.1)$$

can be treated in different ways that will be briefly discussed here.

The algebraic method (Čížek et al 1980, Čížek and Vrscay 1982) seems to be most suitable as it provides an appropriate basis set for the secular equation approach outlined in § 3 (Fernández et al 1984b, 1985a, b). However, if the perturbation potential is more complex, as in the case of the hydrogen-ion molecule (Čížek and Vrscay 1982, Fernández and Castro 1984b) the method of § 2 is preferable.

In this and the following sections we show some new results for the Zeeman effect in hydrogen obtained through the method of § 2. To this end, we try the set of functions $\{F_{M,N}\}$

$$F_{M,N} = r^M \sin^N \theta \cos^t \theta \exp(im\phi - r/n) \qquad (4.2)$$

where $M = 0, 1, \ldots$, $N = 0, 2, \ldots$, $t = 0, 1$, $m = 0, \pm 1, \pm 2, \ldots$, and $n = 1, 2, \ldots$. The moments $A_{M,N} = \langle \Psi|F_{M,N} \rangle$ are easily found to obey (Fernández and Castro 1984b, 1985)

$$[(M - n + 1)/n]A_{M-1,N} = C_{M,N}A_{M-2,N} + \tfrac{1}{2}(N^2 - m^2)A_{M-2,N-2} + \varepsilon A_{M,N} - \tfrac{1}{8}\lambda A_{M+2,N+2} \qquad (4.3)$$

where $C_{M,N} = \tfrac{1}{2}[M(M+1) - (N+t)(N+t+1)]$ and $\varepsilon = E + 1/n^2$. Although this expression holds for all the states of the Hamiltonian operator (4.1), each one has to be treated separately because we have to use the second procedure of § 2.

An alternative recurrence relation is obtained when using

$$F_{N,l} = r^N P_l^M (\cos \theta) \exp(im\phi - r/n) \qquad (4.4)$$

where P_l^M are the Legendre polynomials, $M = |m|$ and $N = 0, 1, \ldots$. In this case the calculation is facilitated by the fact that

$$\sin^2 \theta P_l^M = a_l^M P_{l-2}^M + b_l^M P_l^M + c_l^M P_{l+2}^M \qquad (4.5)$$

where

$$a_l^M = -\alpha_l^M \alpha_{l-1}^M \qquad (4.6a)$$

$$b_l^M = 1 - \alpha_l^M \beta_{l-1}^M - \beta_l^M \alpha_{l+1}^M \qquad (4.6b)$$

$$c_l^M = -\beta_l^M \beta_{l+1}^M \qquad (4.6c)$$

and

$$\alpha_l^M = \frac{l+M}{2l+1} \qquad \alpha_l^M = 0 \text{ if } l < M+1 \qquad (4.6d)$$

$$\beta_l^M = \frac{l-M+1}{2l+1}. \qquad (4.6e)$$

Substitution of (4.4) into (2.2) yields

$$[(N+1-n)/n]A_{N-1,l}$$
$$= \tfrac{1}{2}[N(N+1) - l(l+1)]A_{N-2,l} + \varepsilon A_{N,l}$$
$$- \tfrac{1}{8}\lambda(a_l^M A_{N+2,l-2} + b_l^M A_{N+2,l} + c_l^M A_{N+2,l+2}) \qquad (4.7)$$

where $A_{N,l} = \langle \Psi | F_{N,l} \rangle$. Although both equations (4.3) and (4.7) are suitable for perturbation calculations we find the former more convenient for programming and its use will be illustrated in the following sections.

It must be remembered that the Rayleigh–Schrödinger perturbation expansion for this model is asymptotic divergent (Avron 1981) and therefore an appropriate resummation technique is required to deal with the large-order series (Arteca *et al* 1984 and references therein).

5. Tightly bound states

For the sake of simplicity we use the hydrogen atom quantum numbers ($n = 1, 2, \ldots$, $l = 0, 1, \ldots, n-1$, and $m = -l, -l+1, \ldots, l$) to label the Zeeman states although only m is related to an actual constant of the motion. The tightly bound states ($l = -m = n - 1$) appear to be the most widely studied ones (Gay 1984) and we consider them first. It is well known that perturbation theory for non-degenerate levels can be applied to these states and, in addition to this, they can be treated in a unified fashion through the method of § 2 because their zeroth-order radial parts have no nodes in $0 < r < \infty$ (Fernández and Castro 1985).

When $M = N = n - 1$, equation (4.3), with $t = 0$ and $m = 1 - n$, reduces to $\varepsilon A_{n-1,n-1} = \tfrac{1}{8}\lambda A_{n+1,n+1}$, which suggests the normalisation condition $A_{n-1,n-1} = 1$. To avoid large matrices and obtain only one set of equations for all the tightly bound states it is convenient to define $u = M - n + 1$, $v = N - n + 1$ and $B_{u,v} = A_{M,N}$. This leads to

$$B_{0,0} = 1 \qquad (5.1)$$

$$\varepsilon = \tfrac{1}{8}\lambda B_{2,2} \qquad (5.2)$$

$$B_{u-1,v} = (n/u)\{C_{u+n-1,v+n-1}B_{u-2,v}$$
$$+ \tfrac{1}{2}[v^2 + 2v(n-1)]B_{u-2,v-2} + \tfrac{1}{8}\lambda(B_{2,2}B_{u,v} - B_{u+2,v+2})\} \tag{5.3}$$

where $u = 2, 3, \ldots$ and $v = 0, 2, \ldots, \leqslant u$. The recurrence relation for the perturbation corrections is given by

$$B^{(q)}_{u-1,v} = (n/u)\Bigg(C_{u+n-1,v+n-1}B^{(q)}_{u-2,v} + \tfrac{1}{2}[v^2 + 2v(n-1)]B^{(q)}_{u-2,v-2}$$

$$- \tfrac{1}{8}B^{(q-1)}_{u+2,v+2} + \tfrac{1}{8}\sum_{s=0}^{q-1} B^{(s)}_{2,2}B^{(q-s-1)}_{u,v} \Bigg) \tag{5.4a}$$

$$E^{(q)} = \tfrac{1}{8}B^{(q-1)}_{2,2}. \tag{5.4b}$$

In order to obtain $E^{(p+1)}$ we have to calculate all the elements $B^{(q)}_{u,v}$ where $0 \leqslant q \leqslant p$, $1 < u \leqslant 2 + 3(p-q)$ and $v = 0, 2, \ldots, \leqslant u$.

Equations (5.4) are suitable for numerical calculation (Arteca *et al* 1984, Austin 1984) even with small microcomputers (Fernández and Castro 1985). In this paper we show some algebraic results obtained by means of the REDUCE program (version 3.2). The first five energy perturbation corrections are given below:

$$E^{(1)} = n^3(n+1)/8 \tag{5.5a}$$

$$E^{(2)} = -n^7(12n^3 + 39n^2 + 41n + 14)/384 \tag{5.5b}$$

$$E^{(3)} = n^{11}(216n^5 + 1305n^4 + 3137n^3 + 3748n^2 + 2228n + 528)/9216 \tag{5.5c}$$

$$E^{(4)} = -n^{15}(112\,320n^7 + 1038\,555n^6 + 4151\,305n^5 + 9297\,860n^4 + 12\,597\,304n^3$$

$$+ 10\,314\,342n^2 + 4716\,468n + 926\,640)/4423\,680 \tag{5.5d}$$

$$E^{(5)} = n^{19}(17\,625\,600n^9 + 225\,396\,675n^8 + 1303\,537\,775n^7 + 4476\,434\,750n^6$$

$$+ 10\,056\,564\,084n^5 + 15\,310\,072\,754n^4 + 15\,760\,955\,624n^3$$

$$+ 10\,545\,806\,904n^2 + 4144\,615\,200n + 725\,587\,200)/530\,841\,600. \tag{5.5e}$$

As far as we know they have not been reported before.

6. The 2s state

From a physical viewpoint the 2s state is not as important as those discussed previously. However, since the radial part of the 2s wavefunction exhibits a node it is suitable for illustrating how to deal with the second method developed in § 2.

The appropriate values of n, m and t for the 2s state are easily found to be 2, 0 and 0, respectively, and the general equation (4.3) becomes

$$(M-1)A_{M-1,N} = 2(C_{M,N}A_{M-2,N} + \tfrac{1}{2}N^2 A_{M-2,N-2} + \varepsilon A_{M,N} - \tfrac{1}{8}\lambda A_{M+2,N+2}). \tag{6.1}$$

When $(M, N) = (0, 0)$ and $(1, 0)$, it yields a pair of equations from which $A_{-1,0}$ can be eliminated to obtain $\varepsilon(A_{1,0} - 2A_{0,0}) = \tfrac{1}{8}\lambda(A_{3,2} - 2A_{2,2})$. This suggests the normalisation condition

$$A_{1,0} = 1 + 2A_{0,0} \tag{6.2}$$

which leads to

$$\varepsilon = \tfrac{1}{8}\lambda(A_{3,2} - 2A_{2,2}). \tag{6.3}$$

Notice that equation (6.2) is equivalent to $\langle \Psi | 2s \rangle = 1$, where, disregarding the renormalisation factor, $|2s\rangle = (r-2) e^{-r/2}$.

Equation (6.1) with $M = 2$ and $N = 0$ and equation (6.2) enable one to write

$$A_{0,0} = \tfrac{1}{4}[1 - \tfrac{1}{4}\lambda(A_{3,2} - 2A_{2,2})A_{2,0} - \tfrac{1}{4}\lambda A_{4,2}]. \tag{6.4}$$

Expansion of equations (6.1), (6.3) and (6.4) in powers of λ yields the following recurrence relation for the moment perturbation corrections:

$$A_{0,0}^{(p)} = \tfrac{1}{4}\delta_{p,0} + \tfrac{1}{16}\sum_{q=0}^{p-1}(2A_{2,2}^{(q)} - A_{3,2}^{(q)})A_{2,0}^{(p-q-1)} - \tfrac{1}{16}A_{4,2}^{(p-1)} \tag{6.5a}$$

$$A_{M-1,N}^{(p)} = \frac{2}{M-1}(C_{M,N}A_{M-2,N}^{(p)} + \tfrac{1}{2}N^2 A_{M-2,N-2}^{(p)} + \tfrac{1}{8}\sum_{q=0}^{p-1}(A_{3,2}^{(q)} - 2A_{2,2}^{(q)})$$

$$\times A_{M,N}^{(p-q-1)} - \tfrac{1}{8}A_{M+2,N+2}^{(p-1)}) \qquad M = 2, 3, \ldots, N = 0, 2, \ldots, \leqslant M \tag{6.5b}$$

$$E^{(p)} = \tfrac{1}{8}(A_{3,2}^{(p-1)} - 2A_{2,2}^{(p-1)}) \qquad p > 0. \tag{6.5c}$$

Inspection of equations (6.5) reveals that it is necessary to calculate $A_{M,N}^{(q)}$ for $0 \leqslant q \leqslant p$, $2 \leqslant M \leqslant 3(p-q+1)$ and $N = 0, 2, \ldots, \leqslant M$ in order to obtain $E^{(p+1)}$. The procedure is straightforward and requires no further discussion. Results have been given earlier by Arteca *et al* (1984).

7. Further comments and conclusions

The general formulation of the moment method given in this paper is intended to reveal the great flexibility of the procedure and establish the necessary conditions for its application. It has been argued how to select the most appropriate set of functions $\{F_i\}$ for each problem. In the case of the quantum mechanical oscillators and central-field models the eigenfunctions of H_0 seem to be most convenient because they allow the use of the modified operator method (Fernández *et al* 1984b, 1985a, b) which leads to accurate perturbation series. However, when the calculation of the matrix elements of the perturbation potential is cumbersome, the use of other functions may be advantageous. One of the main conclusions of the present paper is that the secular equation method can be viewed as a particular case of the MPT.

As pointed out before, the Zeeman effect in hydrogen may be best treated through the secular equation method. However, since its application requires resorting to the rather involved SO(4, 2) Lie algebra (Čižek *et al* 1980, Čižek and Vrscay 1982) we preferred the alternative simpler approach of § 2. Results using the modified operator method will be presented elsewhere in a forthcoming paper.

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References

Arteca G A, Fernández F M, Mesón A M and Castro E A 1984 *Physica* A **128** 253
Austin E J 1984 *Int. J. Quantum Chem. Symp.* **18** 449

Avron J E 1981 *Ann. Phys., NY* **131** 73

Blankenbecler R, De Grand T and Sugar R L 1980 *Phys. Rev.* D **21** 1055

Čižek J, Adams B G and Paldus J 1980 *Phys. Scr.* **21** 364

Čižek J and Vrscay E R 1982 *Int. J. Quantum Chem.* **21** 27

Epstein S T 1974 *The Variation Method in Quantum Chemistry* (New York: Academic) p 21

Fernández F M, Arteca G A, Maluendes S A and Castro E A 1984a *Phys. Lett.* **103A** 19

Fernández F M and Castro E A 1982 *Kinam* **4** 193

—— 1984a *Match* **15** 133

—— 1984b *Int. J. Quantum Chem.* **26** 497

—— 1985 *Int. J. Quantum Chem.* **28** 603

Fernández F M, Mesón A M and Castro E A 1984b *Phys. Lett.* **104A** 401

—— 1985a *Phys. Lett.* **111A** 104

—— 1985b *Phys. Lett.* **112A** 107

Gay J C 1984 *Progress in Atomic Spectroscopy* ed H J Beyer and H Kleinpoppen (New York: Plenum) part C

Killingbeck J and Jones M N 1986 *J. Phys. A: Math. Gen.* **19** 705

Killingbeck J, Jones M N and Thompson M J 1985 *J. Phys. A: Math. Gen.* **18** 793

Swenson R J and Danforth S H 1972 *J. Chem. Phys.* **57** 1734