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# A multiple shooting method for the Zeeman effect

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## Abstract

A multiple shooting procedure in coupled angular momentum spaces is used to calculate the Zeeman energy levels of the hydrogen atom. The method is found to deal efficiently with the low field splittings of initially degenerate states, including some Rydberg states.

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## 1. Introduction

In a recent work we have shown that a multi-purpose iterative moment algorithm can be used to calculate the perturbed energy levels of a hydrogen atom in both electric and magnetic fields [1]. Because the moment method used a particularly simple type of basis function it was only able to deal with a restricted family of non-degenerate states, although for these states it produced results of high accuracy. For the case of the Zeeman effect the method could deal with the 3d states of magnetic quantum numbers  $\pm 1$  and  $\pm 2$ , but not with the 3d state of magnetic quantum number 0, since that state is coupled by the magnetic field operator to the 3s state, with which it is initially degenerate. On seeking a simple way to deal with the Zeeman effect for such degenerate states we noted that two methods published years ago can be developed to give an efficient approach to the problem.

If the simple additive spin and orbital terms are omitted then we can take the non-relativistic Hamiltonian (in atomic units) for the problem in the form

$$H = -(1/2)\nabla^2 - Z/r + (\gamma^2/8)(x^2 + y^2). \quad (1)$$

The decomposition  $x^2 + y^2 = (1/3)[2r^2 - (3z^2 - r^2)]$  splits the magnetic field term into components with angular momentum  $L = 0$  and  $L = 2$ , respectively. Using the  $L = 0$  magnetic field operator  $\gamma^2 r^2/12$  alone gives the spherical field approximation [2, 3]. This is a good approximation for s states in weak fields, since a magnetic field of 50 T is about the limit for a terrestrial magnet and yet only corresponds to a  $\gamma$  value of 0.000 213. A spherical approximation is still possible for non-s states. If the expectation value of  $(x^2 + y^2)$  is  $F(L, M)\langle r^2 \rangle$  for a state with the angular momentum quantum numbers  $L$  and  $M$ , then the operator

$(\gamma^2/8) F(L, M)r^2$  serves as the radial operator to be used in the spherical approximation. The rest of the magnetic field operator gives zero energy shift in first order and so for weak fields we can estimate the energy by solving the Schrödinger equation for a hydrogen atom with a radial perturbing field. For the initially degenerate 3s and 3d<sub>0</sub> states the two states have  $F(L, M)$  which differ slightly. The 3d<sub>0</sub> one (5/84) is smaller than the 3s one (1/12) and the value of  $\langle r^2 \rangle$  is also less for the 3d<sub>0</sub> state, so that in lowest order the 3d<sub>0</sub> state has a lower energy than the 3s state. Thus the spherical approximation of [2, 3] predicts a splitting of the originally degenerate level even before we turn on the terms in the potential which couple the two states and convert the wavefunction into a linear combination of the nominally 3s and 3d wavefunctions. What the radial effective potential does is to account for the coupling to all other states of the same angular momentum as the initial state (including continuum states). Turning on the residual interaction produces a repulsion between the close partners in the split level and so the order of the levels in the 3d–3s pair remains as predicted by the spherical model. To work out how the splitting actually increases with the magnetic field strength we need a detailed calculation which takes into account all the coupling between states of several different angular momenta which is produced by the  $L = 2$  term in the magnetic field operator.

In [4] a method was produced which could handle the problem. However, as presented in [4] the method involved very slow calculations, which can best be explained by describing a typical example. To calculate the energy of a 1s state a speedy shooting calculation was carried out along the  $L = 0$  column of an array to find an approximate energy (based on the spherical approximation). A slow diffusion/relaxation process was then carried out along the network of array columns corresponding to the other angular momenta, which were coupled to the  $L = 0$  column by the  $L = 2$  terms in the magnetic field operator. The back coupling from the other columns to the  $L = 0$  column then changed the eigenvalue produced by the shooting process and so on. After a long time the whole network settled down to an equilibrium distribution of values and the shooting eigenvalue stabilized at the perturbed energy. In [4] only single precision calculations were performed. It has now been found how to improve the original calculational method by performing speedy shooting along all the columns. The resulting improvement in the calculations makes it feasible to obtain energies of high accuracy when double precision is used.

In section 2 we describe the method of calculation. Section 3 then gives a simple example to show how the method can indicate the effect on the energy of including more angular momentum states in the basis set. Section 4 deals with degenerate states arising from levels with principal quantum numbers 3, 4 and 5. Section 5 presents some recent results for Rydberg states.

A brief appendix gives more detail about the computational method.

## 2. The basic recurrence relations

Much of the basic theory was already presented in [4] but for completeness we give a brief summary of the results here. We expand the perturbed wavefunction in the form

$$\psi = \sum_{N,L} W(N, L) \exp(-\beta r) r^N Y_L^M(\theta, \phi), \quad (2)$$

where  $Y_L^M(\theta, \phi)$  is an unnormalized spherical harmonic which is the product of a factor  $\exp(iM\phi)$  and an associated Legendre polynomial  $P_L^M(\mu)$  [4]. We now act on this postulated wavefunction with the Hamiltonian in equation (1), noting that the term  $x^2 + y^2$  can be written as  $r^2(1 - \mu^2)$ . Since all of the other terms are spherically symmetric it is the second part of this term which couples the different angular momentum terms appearing in the wavefunction,

while the kinetic energy operator and the various powers of  $r$  in the Hamiltonian produce couplings which increase or decrease the power of  $r$ . Proceeding in the spirit of a Hill determinant calculation we can extract the coefficient of the typical term shown in (2) and obtain the recurrence relation

$$\begin{aligned} 1/2(N+2-L)(N+3+L)W(N+2, L) &= [(N+2)\beta - Z]W(N+1, L) \\ &\quad - [E + \beta^2/2]W(N, L) + \lambda[D(L)W(N-2, L) \\ &\quad + A(L+2)W(N-2, L+2)] + B(L-2)W(N-2, L-2)], \end{aligned} \quad (3)$$

where  $\lambda = \gamma^2/8$  and the coefficients arising from the angular momentum coupling are

$$A(L) = \frac{-(L+M)(L+M-1)}{(2L+1)(2L-1)} \quad (4)$$

$$B(L) = \frac{-(L+1-M)(L+2-M)}{(2L+1)(2L+3)} \quad (5)$$

$$D(L) = -A(M, L) - B(M, L). \quad (6)$$

Here a warning about notation is necessary. To simplify the equations the magnetic quantum number  $M$ , which is invariant throughout a particular calculation, is omitted from the symbols. For example an extra identical  $M$  symbol in every term of (3) would simply complicate the equation and would be essentially redundant in terms of providing extra information. More of the mathematical steps used in the derivation of (3) can be found in [4]. In the present work we concentrate on the specific task of extracting the perturbed eigenvalues from (3).

We first impose the constraint that  $W(N, L)$  is zero for  $N < L$  (so as to retain only regular wavefunctions) and that it is also zero for  $N > NU$  ( $N$  upper) where  $NU$  is some large integer which we use to keep a finite basis set.  $L$  will also have an upper value  $LU$  ( $L$  upper), which will be increased gradually to study the effects of including more angular momenta into the basis set. If the  $A$  and  $B$  terms are omitted then the resulting problem becomes that for the effective spherical potential introduced in [1].

To treat the full Zeeman problem we turn on the  $A$  and  $B$  terms in (3) and set up a large array with rows being labelled by  $N$  and columns by  $L$ . To find, for example, the perturbed energy arising from the  $2p_0$  state we use the initial trial energy  $-0.125$ , set  $M = 0$  in all terms and calculated coefficients and shoot along the  $L = 1$  column to find the energy for which we have  $W(NU, 1) = 0$ . This gives us the spherical approximation result. We next shoot along the  $L = 3$  column, not to find the energy but to find the column of  $W(N, 3)$  values which gives  $W(NU, 3) = 0$  in the presence of the coupling to the set of  $W(N, 1)$  values which has just been established. Shooting along the  $L = 1$  column now gives a shifted energy and so on. After a few cycles the values in the  $L = 1$  and  $L = 3$  columns settle down, as does the calculated energy.  $NU$  can be gradually increased to ensure that we have included plenty of radial functions to reach the correct limit for each of the two angular momenta. The final result will then be the best energy obtainable using a basis set of  $L = 1$  and  $L = 3$  functions. This result is universal, in the sense that it will also be valid for conventional matrix calculations using basis sets. To extend the range of coupled angular momenta we include the  $L = 5$  column in the cycle of shooting calculations, and so on. As the values of  $NU$  and  $LU$  are increased we eventually reach a limiting energy which is the best (lowest) one and can be taken to be the required Zeeman energy. This method of calculating makes quite visible the role played by the basis functions of a particular angular momentum.

The role of the variable parameter  $\beta$  merits a separate discussion. In the calculations  $\beta$  was adjusted empirically so as to ascertain how its value affected the progress of the calculation.

**Table 1.** The multiple shooting energies of the 1s hydrogen groundstate as a function of the maximum  $L$  value allowed in the basis functions. The values  $\gamma = 0.3$  and  $\beta = 2.0$  were used throughout.

$L$	$E$
0	-0.478 928 499 7381
2	-0.479 185 586 0309
4	-0.479 186 544 1567
6	-0.479 186 552 7657
8	-0.479 186 552 8985
10	-0.479 186 552 9014
12	-0.479 186 552 9015

It was found that as  $\beta$  varies the  $NU$  value, i.e. the number of radial terms needed to saturate the contribution from each  $L$  component, increases or decreases.  $\beta$  was accordingly adjusted by trial and error so as to achieve the limiting energy for a given set of  $L$  columns with a reasonably small (not necessarily minimum)  $NU$  value. It was found that for very small fields the ‘natural’ (zero field)  $\beta$  value  $1/n$  (for principal quantum number  $n$ ) is satisfactory but that as  $\gamma$  increases the  $\beta$  value needed to obtain stable and quickly converging results (as  $NU$  and  $LU$  increase) becomes much larger than the zero-field value. In the tables we give the  $\beta$  value used (although a range of values around the cited value will serve equally well). Since the values of the  $W(N, L)$  vary by many orders of magnitude throughout the array it is an advantage to set the initial and fixed value of  $W(L_0, L_0)$  as a large number when studying states of (unperturbed) angular momentum  $L_0$ ; this helps to avoid underflow as that initial value diffuses out through the network to give all the other  $W(N, L)$  their correct relative values. A value as large as  $10^{50}$  was found to work satisfactorily. A more subtle procedure involving a scaling factor such as  $K^{(N+L)}$  was also built into our program but the simple device of using a large  $W(L_0, L_0)$  sufficed to obtain the results presented in this paper. To start off the first shooting calculation for the chosen angular momentum it is necessary to use an input energy estimate. Since for the chosen angular momentum (which we denote by  $L_0$ ) there will be many possible unperturbed energies, the best procedure for weak magnetic fields is to use the initial value  $-1/(2n^2)$  so as to pick out the zero-field state with principal quantum number  $n$ . The method has a tendency to ‘lock on’ to the state with the specified  $L$  and  $M$  which is nearest in energy to the initially given energy; this is, of course, a common behaviour in shooting methods.

### 3. The variation of $E$ with basis size

As an example of how the multiple shooting method works in practice we present in table 1 what happens when the number of participating  $L$  components is increased for the case of the 1s state at a field strength  $\gamma = 0.3$ . The  $NU$  value was increased from 20 to 60 in steps of 10 to check that the limiting values for the  $L$  columns are reached. Since we only used normal double precision there was some degree of fluctuation in the last decimal digits but the stability attained was good enough to give 13 digit energies, as established by several test calculations in which existing results from the literature and from the method of [1] gave reference energies. Table 1 shows that to obtain 13 digit accuracy for this case it is necessary to include basis functions up to  $L = 12$  and this conclusion will be valid for any matrix diagonalization method using ordinary basis states.

**Table 2.** The energies of the two coupled states with  $M = 0$  arising from the  $n = 3$  degenerate level of hydrogen. The energy of the state with zero-field label 3s is given first, followed by that of the state with zero-field label 3d. The  $\beta$  value of 0.4 sufficed for the first three small  $\gamma$  values, a  $\beta$  value of 1–1.3 was used for the remaining  $\gamma$  values. The five or six digit results of [5] agree with those from the multiple shooting method.

$\gamma$	$E(3s,3d)$
0.0005	–0.055 550 661 426 2433 –0.055 554 262 747 8249
0.001	–0.055 535 985 023 4166 –0.055 550 385 087 0114
0.002	–0.055 477 368 745 8426 –0.055 534 885 846 4327
0.010	–0.053 669 329 575 3116 –0.055 047 921 912 9920
0.02	–0.048 634 233 895 344 –0.053 616 935 468 314
0.03	–0.041 533 175 335 356 –0.051 444 850 277 11
0.04	–0.033 280 283 364 89 –0.048 695 382 199 87

#### 4. Calculations for degenerate states

As stated in the introduction, the main point of our calculations is to see how the multiple shooting method can handle degenerate states. To treat the 3s and 3d<sub>0</sub> states we require a set of even  $L$  values, which we take as running from 0 to 20 in steps of 2 (although less than 20 would suffice for the low  $\gamma$  values). To pick out the  $n = 3$  states we use  $-0.05$  as the initial energy and set  $M = 0$ . The only difference between the two states is that for 3s the  $L = 0$  column is reserved for the energy shooting, while for the 3d<sub>0</sub> state it is the  $L = 2$  column which is used. By letting  $NU$  increase from 70 to 90 to ensure that limiting values were reached we obtained the results shown in table 2. We checked that our results agree with those of [5] to the five or six digits given in [5] (after suitable rescaling of the results of [5]). It is clear that the multiple shooting method gives highly accurate results. Table 3 shows our results for the four degenerate states with  $M = 0$  which arise from the  $n = 4$  level of hydrogen. For the p and f states the  $L$  values are, of course, odd integers rather than even integers. In the tables we give some results for very small  $\gamma$  values so as to permit the numerical extraction of perturbation coefficients. Thus for example if we write the low field energy of a state of principal quantum number  $n$  as

$$E(\gamma) = -1/(2n^2) + E_1\gamma^2 + E_2\gamma^4 + \dots \quad (7)$$

we can extract from the low field data the results  $E_1(3d_0) = 5.171\,485\,23$  and  $E_1(3s_0) = 19.578\,5147$ . For the set of states with  $M = 0$  and  $n = 4$  we obtained the numerical values  $E_1(4s_0) = 65.323\,798$ ,  $E_1(4p_0) = 38.649\,109$ ,  $E_1(4d_0) = 18.676\,192$ ,  $E_1(4f_0) = 13.350\,888$ . The state labels, of course, are zero field ones but the actual wavefunctions will be linear combinations of the initial  $LM$  types. However, the ranking of energies implied by these  $E_1$  values is that which results from the spherical approximation splitting which appears before the inter-state coupling is turned on and for which each state retains its original angular momentum labels. Grozdanov and Taylor [6] obtained analytic results for  $E_1$  and  $E_2$  for some low-lying

**Table 3.** The energies of the four states with  $M = 0$  arising from the  $n = 4$  degenerate level of hydrogen. The energies are given in the order of increasing angular momentum (4s,4p,4d,4f). The  $\beta$  value used gradually increased from 0.3 to 0.6 as  $\gamma$  increased.

$\gamma$	$E(4s,4p,4d,4f)$
0.0005	-0.031 233 677 625 1581
	-0.031 240 342 428 1327
	-0.031 245 333 063 3010
	-0.031 246 663 000 0866
0.001	-0.031 184 812 793 3940
	-0.031 211 425 901 9023
	-0.031 231 357 483 0846
	-0.031 236 660 642 5498
0.002	-0.030 990 851 407 4946
	-0.031 096 586 351 1385
	-0.031 175 827 349 0101
	-0.031 196 779 265 7276
0.004	-0.030 236 982 912 9948
	-0.030 649 539 952 9025
	-0.030 959 302 558 9110
	-0.031 039 210 936 2615
0.008	-0.027 490 731 009 7609
	-0.029 017 858 800 5190
	-0.030 165 791 508 2648
	-0.030 435 762 137 9031

degenerate states. Our quoted results for  $E_1$  are in close agreement with the exact results given in [6], as are our rough estimates of  $E_2$ , which gives us confidence in the accuracy of the numerical accuracy of our multiple shooting approach, particularly since we did not find the results of [6] until after making our numerical estimates. For the  $n = 3$  and  $n = 4$  calculations we only have to deal with two-fold splittings of the  $M = 0$  levels (e.g the  $L$  pairs (0, 2) and (1, 3) for  $n = 4$ ). For  $n = 5$ , however, the three-fold splitting of type (0, 2, 4) appears. We found that the iterative shooting method of this paper has a strong tendency to move towards the highest and the lowest levels in a group of split states. Thus for the (0, 2, 4) family it tends to give the 0 and the 4 levels but is difficult to stabilize when the  $L = 2$  level is sought. To avoid this incomplete description of the splitting we have studied the  $M = 1$  splitting, for which the appropriate  $L$  families are (1, 3) and (2, 4). Table 4 thus shows the  $n = 5$  splittings results for the states with  $M = 1$ . Only the five or six digit results of [5] seem to be readily available in the literature and our results are in accord with them, while giving greater accuracy.

## 5. An interesting Rydberg state example

When dealing with excited states the multiple shooting method as presented here should be regarded as appropriate for weak fields, since it is only guided towards a particular state (of the specified  $LM$  type) by giving the initial energy of the region in which to search. For a strong field the calculation might collapse to the lowest eigenvalue of the desired type, although this effect can be diminished by building up the field slowly and following the trajectory of a particular zero-field state. For the lowest state in an  $LM$  family this possibility of collapsing is in any case not present and so strong fields can be handled (for example the case  $\gamma = 1$  for the ground state, where setting  $\beta = 5$  leads to the result  $E = -0.331\ 168\ 896\ 733$ ). As noted

**Table 4.** The Zeeman energies for the  $n = 5$  states with  $M = 1$ . The value of  $\beta$  used increased from 0.2 to 0.4 as the value of  $\gamma$  increased. The linear Zeeman term  $\gamma M/2$  has been included in the displayed energies.

$L$	$\gamma$	$E$
1	0.0005	-0.019 709 848 482 093
	0.001	-0.019 340 288 704 072
	0.002	-0.018 374 456 593 161
	0.004	-0.015 665 928 528 153
	0.008	-0.012 223 879 921 212
2	0.0005	-0.019 723 642 944 629
	0.001	-0.019 395 132 859 622
	0.002	-0.018 588 962 761 991
	0.004	-0.016 465 799 604 409
	0.008	-0.014 923 952 064 118
3	0.0005	-0.019 734 002 958 254
	0.001	-0.019 436 305 947 552
	0.002	-0.018 749 681 586 250
	0.004	-0.017 058 093 939 757
	0.008	-0.016 813 515 251 206
4	0.0005	-0.019 738 913 574 790
	0.001	-0.019 455 760 089 764
	0.002	-0.018 824 663 656 722
	0.004	-0.017 321 131 161 145
	0.008	-0.017 526 270 049 135

in section 1 the strongest terrestrial magnets give a magnetic field corresponding to a  $\gamma$  value of about 0.000 213.

However a  $\gamma$  value of 0.000 02 (about 4.7 T) is more typical and it was this value which was used in two studies of the  $n = 23$  Ryberg states of the hydrogen atom [7, 8]. The calculations of those two works used large basis sets in a more traditional kind of method and so were able to give a list of the many states in the  $n = 23$  manifold together with their perturbed energies. It was thus amusing and surprising to find that the simple approach of the present work was able to locate a subset of the states described in [7, 8], by giving (as noted in section 4) the highest and lowest states in each group of states arising from the splitting of a degenerate level.

The unperturbed energy of the  $n = 23$  manifold is close to  $-0.000 945$  and so specifying this as the initial trial energy with  $\gamma = 0.000 02$  would be the straightforward way to apply the present method to the  $n = 23$  manifold. We tried this procedure, varying the  $LM$  angular momentum type. Table 4 shows the results. The energies obtained for the restricted subset of states attainable by our method are much more accurate than those of [7] and are in accord with the results of high accuracy given in [8], although we can obtain results for some families of states which did not appear in the tables of [7] and [8]. We suspect from our results that the labels 1+ and 1- in the tables of [8] are accidentally transposed. We also note that the energy units used in [8] are Rydbergs rather than the atomic units used here and in [7]. Of particular interest are the near degeneracies between some pairs of states which were found to have the same energy in [7] but which are shown to have a very small but nonzero splitting by our calculation and by the method of [8]. This near—degeneracy for high  $n$  values has been explained in terms of an effective potential of double well form, with small splitting between



**Table 5.** The Zeeman levels for the hydrogen  $n = 23$  level as given by the multiple shooting method for  $\gamma = 0.000\,02$ , with  $\beta$  values  $0.045\text{--}0.06$  and an initial energy of  $-0.000\,94$ . The chosen  $(M, L_0)$  pair is shown together with the resulting Zeeman energy. The linear shift  $\gamma M/2$  has been included in these energies.

$(M, L_0)$	$E$
(0,0)	-9.123 506 848 480
(0,1)	-9.438 673 731 165
(0,2)	-9.438 673 731 579
(0,3)	-9.148 927 987 648
(1,1)	-9.023 890 526 272
(1,2)	-9.049 305 222 916
(1,3)	-9.326 595 760 590
(1,4)	-9.326 595 778 585
(2,2)	-8.925 041 500 452
(2,3) <sup>a</sup>	-9.150 436 864 937
(2,4)	-9.415 572 242 009
(2,5) <sup>a</sup>	-9.415 571 881 452
(3,3) <sup>a</sup>	-9.126 959 593 457
(3,4) <sup>a</sup>	-9.152 322 722 308
(3,5) <sup>a</sup>	-9.405 613 344 457

<sup>a</sup> Energies for states not covered by the works [7, 8]. Note the near-degeneracies for three pairs of states with the same  $M$ . These states are degenerate at the level of precision used in [7]. The energies are shown in units of  $10^{-4}$  atomic units.

**Table 6.** The variation of the  $[(0, 1), (0, 2)]$  degeneracy with the principal quantum number  $n$  for  $\gamma = 0.00002$ , with  $\beta = 1/n$  and trial energy  $-1/(2n^2)$ . The splitting has a sign which alternates between successive  $n$  values and a magnitude which decreases as  $n$  increases. The energies are shown in units of  $10^{-3}$  atomic units.

$n$	$E(0,1), E(0,2)$
16	-1.952 681 530 420 31 -1.952 681 519 539 02
17	-1.729 571 259 331 87 -1.729 571 264 608 01
18	-1.542 577 306 751 83 -1.542 577 304 249 05
19	-1.384 297 490 434 31 -1.384 297 491 595 25
20	-1.249 132 545 580 47 -1.249 132 545 054 53
21	-1.132 783 729 081 67 -1.132 783 729 313 89
22	-1.031 906 530 740 63 -1.031 906 530 641 01

even and odd parity energy levels [9, 10]. Table 6 shows the variation of one of these level splittings as a function of  $n$ , as found by the multiple shooting method of this work.

## 6. Conclusion

This short work is intended to show that the multiple shooting method is an effective way of handling the weak field Zeeman problem for degenerate excited states of the hydrogen

atom. The approach can be regarded as a Hill determinant one in the spirit of those matrix methods which use a non-orthogonal basis set. Our basis set is equivalent to the Sturmian basis set used in [7], except that in [7] the basis set was used in the traditional manner, thus leading to a generalized matrix eigenvalue problem which needed the evaluation of matrix elements and overlap integrals. Alternatively, our multiple shooting method can be regarded as a discretized approach to solving the coupled family of differential equations used to treat the field-induced coupling of angular momenta in the works [5, 11]. Although we have given only a few specimen results to indicate the level of accuracy which can be achieved, it is clear that the present method has some of the flexibility of the recently published moment method [1], plus the ability to handle states which are not accessible to that method. For example, it is clearly a simple task to add another term to the recurrence relation (3) to represent an extra term  $\alpha r^2$  in the applied field. By using an appropriate sum of  $r^2$  and  $x^2 + y^2$  we can treat the static Van der Waals interaction  $-\lambda (r^2 + z^2)$  as in [1], or by adding a very small increment to a term in the Hamiltonian we can calculate expectation values by energy differencing as in [1].

The multiple shooting calculation for the 3s–3d splitting was first carried out in 1999 at the Observatory of Besancon by one of the authors (JPK). The present extension of the method was developed recently in order to extend the iterative type of calculation used in [1] so as to treat a larger range of states, both degenerate and non-degenerate. Since the intention of the authors is to encourage other workers to apply and develop the approach described here, an appendix is added to explain in more detail how the multiple shooting process is actually implemented.

### Appendix The basic principles of the multiple shooting method

The aim of the shooting calculation is to find the value of  $E$  when shooting along the  $L = L_0$  column and to find  $W(L, L)$  when shooting along any other  $L$  column. Once the value of  $W(L, L)$  is found of course, the other elements  $W(N, L)$  are automatically filled in by the shooting process. The basic quantities required are the derivatives of the  $W(N, L)$  with respect to  $E$  for the  $L_0$  column and to  $W(L, L)$  for the other columns. An economical way to proceed is to call both derivatives  $WE(N, L)$ , with their interpretation and use varying according to whether or not  $L$  equals  $L_0$ . Thus only one array is set up for the derivatives. The calling program for the shooting subroutine sends an index  $I$  which is 1 for  $L = L_0$  and 0 for any other  $L$ . The  $WE$  recurrence relation is found by differentiating equation (3) of the text while remembering that for shooting along the  $L$  column we must only perform the differentiation on terms which have the second index  $L$ . The resulting recurrence relation thus becomes

$$\begin{aligned} 1/2(N+2-L)(N+3+L)(N+2, L) &= [(N+2)\beta - Z]WE(N+1, L) \\ &- [E + \beta^2/2]WE(N, L) + \lambda D(L)WE(N-2, L) - I.W(N, L), \end{aligned} \quad (A1)$$

(note how the factor  $I$  is used to change between the two types of derivatives). This enables the  $W(N, L)$  and the  $WE(N, L)$  columns to be found together by shooting along the  $L$  column, starting with  $W(L-1, 1) = 0$  in all cases and with  $W(L, L)$  equal to 0 initially for  $L$  not equal to  $L_0$  or to the large chosen fixed value when  $L = L_0$ .  $WE(L, L)$  is 0 for  $L = L_0$  and 1 for all other  $L$  values. The value of  $W(NU, L)$  is returned to the main program, which then works out a Newton's method shift given by the ratio  $SH = -W(NU, L)/WE(NU, L)$ . This shift is then used to find the change in  $E$  if  $L = L_0$  or in  $W(L, L)$  for any other  $L$ . For the  $E$  calculation it is useful to use a 'maximum shift' parameter  $SHM$  to keep the calculation stable on a particular level. The shift as calculated above is then replaced by  $SH/[1 + ABS(SH/SHM)]$ , which damps down the amplitude (but not the direction) of the shift. Several successive shootings

are performed along the column until the calculated  $E$  or  $W(L, L)$  has converged. The tactics of the shooting process is to some extent a matter of choice. For example, we can decide how many  $L$  columns to include in the process at any stage, although experience suggests that the number of included columns should be increased gradually, so that the calculated eigenvalue slowly changes towards its final ‘saturated’ value when all necessary  $L$  subspaces have been included. The  $NU$  value can either be increased slowly or left at some sufficiently high value determined by a preliminary trial computation. The set of coefficients  $A(L)$ ,  $B(L)$  and  $D(L)$  can be worked out at the start of the calculation and stored so as to be immediately available when needed during the shooting process along any column.

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