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Abstract
A simple moment method is used to treat some low-lying states of the hydrogen atom. Accurate results are obtained for the Stark effect, the Zeeman effect and for the energy shifts due to several mixed perturbations.

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1. Introduction

The present work describes a simple moment calculation which can deal with both resonant states and bound states produced by electric and magnetic fields for some low-lying states of the hydrogen atom. Most of the traditional literature applies methods specifically designed for either the Stark or the Zeeman effect, while the method of the present work is a multi-purpose one. The most detailed developments and applications of moment techniques in the literature are those due to C R Handy and his collaborators. To deal with systems which can yield complex eigenvalues they applied a moment approach to a special equation involving the squared modulus of the wavefunction [1, 2]. They also treated the ground state hydrogen atom Zeeman effect by a moment method, after making a transformation to parabolic coordinates [3]. In matrix approaches to the Stark effect probably the best trailed idea is that of complex scaling, which was applied in a series of similar papers long ago [4–6]. One of the clearest reviews of the matrix approach to resonances is that of Moiseyev [7], in which it was proposed that a complex form of the hypervirial relations should be valid even for resonant state wavefunctions. In recent years this idea has been followed up in detail and hypervirial perturbation theory has been given a complex extension which yields accurate complex resonant state energies for several model systems previously treated by more complicated methods [8]. The Hill-series method has also been found to be capable of complex extension to give resonant state energies for some systems [9]. These latter two techniques have the special feature that they involve no direct use of a wavefunction. It thus appears that the earlier methods involving wavefunctions and complex matrix diagonalizations are part of a more general scheme which can be described

as follows. We start with a technique which works for bound state problems but which contains a nonlinear parameter (e.g. an effective nuclear charge or an effective oscillator frequency). We then give a complex value to that parameter and use complex arithmetic in the calculations. This yields complex energies which refer to the resonant states of the system. The aim of the present work is to demonstrate that yet another traditional method, the simple method of moments, also conforms to this pattern and so can give resonant states when an effective nuclear charge is given complex values. The usual moment approach which has been applied to the Stark or Zeeman effect is to pass through the moment equations (without using them directly) in order to construct a perturbation theory [10–12]. We believe that the present work is the first one to attempt a direct multi-purpose numerical application of the most simple spherical polar moment equations to the Stark, Zeeman and other effects for the hydrogen atom. The numerical results obtained are of high accuracy and in most cases are as good as those obtained by previous works dedicated to a specific effect. Section 2 presents the basic moment recurrence relation. Section 3 explains the efficient calculational use of the relation. Sections 4 and 5 present numerical calculations for the Stark and Zeeman effects. Section 6 treats a variety of unusual potentials and section 7 gives a brief discussion and conclusion.

2. The basic moment secular equation

We study the Schrodinger equation (in atomic units)

$$H\Psi = \left[-\frac{1}{2}\nabla^2 - \frac{Z_o}{r} + V \right]\Psi = E\Psi \tag{1}$$

where the perturbing potential is of the form

$$V = \sum_{J,K} V(J,K) r^J \mu^K \tag{2}$$

with $\mu = \cos(\theta)$. The indices J and K run from 0 to 2, which allows for most of the traditional perturbations usually studied for the hydrogen atom. To simplify the analysis we use reference functions $\Phi(N,M)$ of the form

$$\Phi(N,M) = \exp(-Zr)(x+iy)^L r^N \mu^M \tag{3}$$

where Z is an adjustable parameter. The factor $(x+iy)^L$ is a harmonic function. This simplifies the use of the kinetic energy operator. To apply the standard moment approach we evaluate the terms in the equation

$$\langle \Phi(N,M)|H|\Psi \rangle = \langle \Psi|H|\Phi(N,M) \rangle = E\langle \Phi(N,M)|\Psi \rangle \tag{4}$$

Evaluating the second and third terms in (4), with $A(N,M) = \langle \Phi(N,M)|\Psi \rangle$, gives the recurrence relation

$$C(N-1,M)A(N-1,M) + C(N-2,M)A(N-2,M)$$
$$+ C(N-2,M-2)A(N-2,M-2) + \sum_{J,K} V(J,K)A(N+J,M+K)$$
$$= [E + Z^2/2]A(N,M) \tag{5}$$

where

$$C(N-1,M) = Z(N+1+L) - Z_0$$
$$C(N-2,M) = \tfrac{1}{2}[M(M+1+2L) - N(N+1+2L)]$$
$$C(N-2,M-2) = -\tfrac{1}{2}M(M-1).$$

The standard approach in the literature would next expand the $A(N,M)$ and the energy as power series in one (or more rarely two) of the perturbation parameters so as to produce

recurrence relations which would eventually lead to the construction of a single (or double) perturbation series for the energy E. This approach necessarily requires the use of arrays with three or more indices, involving increased computer memory space. This increased memory requirement will often limit the order of perturbation theory which can be attained and thus limit the accuracy of the numerical results, even when some summability technique is used to treat the perturbation series for E (which will often turn out to be divergent). In the present work we treat the moment equation (5) directly as a secular equation. This requires much less memory space and makes possible an iterative solution process which gives more accurate results than the perturbation form of the calculation.

In the present work we treat five non-degenerate states which have a single $\Phi(N, M)$ as their unperturbed wavefunction and for which the perturbed wavefunction can be expressed as a linear combination of the $\Phi(N, M)$. Since the unperturbed wavefunctions all have equal M and N indices we can use the label (L, M_0) for the unperturbed states. The five states studied are $1s_0(0, 0)$, $2p_0(0, 1)$, $2p_1(1, 0)$, $3d_1(1, 1)$ and $3d_2(2, 0)$.

3. The general method of calculation

To treat the state (L, M_0) we set $A(M_0, M_0) = 1$ and keep this value fixed throughout the calculation. The L value is then used in evaluating the coefficients in the recurrence relation (5). The value of Z has to be adjusted empirically to obtain the best results; the details depend on the potential V and so are treated case by case in later sections of the discussion. As presented above, equation (5) is in typical matrix eigenvalue form, with the unknown energy on the right. To carry out the major part of the iterative process we rewrite equation (5) so as to express $A(N - 1, M)$ in terms of all the other quantities. To initiate the iterations we set E at the unperturbed energy for the appropriate state, which is $(-1/2n^2)$ for the case of principal quantum number n. The values of a sequence of $A(N - 1, M)$ are then calculated by scanning the indices as follows: M goes from M_0 to some maximum value MU; at a given M the index N varies from M up to a maximum value NU, except that for $M = M_0$ the index N varies from $M_0 + 2$ to NU. (The case $M = M_0$, $N = M_0 + 1$ obviously has to be avoided, since it would change the fixed value $A(M_0, M_0) = 1$.) Here the assigned integers MU and NU (M upper and N upper) are the upper limits which are essentially determining how many radial and angular terms are being allowed to contribute to the wavefunction. At each point of the scan over the indices we will have the existing $A(N - 1, M)$ value and the newly calculated value $AC(N - 1, M)$. To aid convergence of the iterative process we found it useful to introduce a relaxation parameter RA, such that the new $A(N - 1, M)$ value is taken to be $A(N - 1, M) + RA[AC(N - 1, M) - A(N - 1, M)]$. Inspection of equation (5) shows that to evaluate E (on the right) we need $A(M_0 - 1, M_0)$, which has been specifically omitted from our scan, since it would correspond to the case $M = N = M_0$. To find $A(M_0 - 1, M_0)$ we use another rewriting of equation (5) in which the $A(N - 2, M)$ term is expressed in terms of all the other quantities. We can then set $M = M_0$, $N = M_0 + 1$ in this equation to yield a result for $A(M_0 - 1, M_0)$. Returning to the original form of equation (5) we can now set $M = N = M_0$ to obtain a new computed energy value EC. We again use a relaxation parameter, denoted by RE, taking the revised energy value to be $E + RE[EC - E]$. We note that both RA and RE can be kept real, even for the case of the complex energies which occur in Stark effect calculations.

Since it is our intention to make the algorithm sufficiently clear for readers to be able to use it, we supplement the algebraic description given above by a more program-based version. We represent equation (5) term by term in the schematic form $T1 + T2 + T3 + TV = TE$, supposing that a subroutine has been written which works out the five required terms when

the main program sends the values of M and N. (We note that one of the five is redundant at each call but this can be ignored to simplify the subroutine program.) The three stages of the calculation can then be described as follows (with := here denoting an assignment statement).

(i) The $A(N-1, M)$ calculations (index range as described previously)

$$R := (TE - T2 - T3 - TV)/C(N-1, M)$$
$$A(N-1, M) := RA \times R + (1 - RA) \times A(N-1, M) \tag{6}$$

(For each M, the scan over N is halted as soon as a zero R value is found.)

(ii) The $A(M_0 - 1, M_0)$ calculation. $[N = M_0 + 1, M = M_0]$

$$R := (TE - T1 - T3 - TV)/C(N-2, M)$$
$$A(M_0 - 1, M_0) := RA \times R + (1 - RA) \times A(M_0 - 1, M_0). \tag{7}$$

(iii) The energy calculation $[N = M = M_0]$

$$EC := T1 + T2 + T3 + TV - Z^2/2$$
$$E := RE \times EC + (1 - RE) \times E. \tag{8}$$

For the Stark effect calculation, of course, the quantities are complex numbers, with a real and an imaginary part, and so complex arithmetic must be used.

Computational trials showed that the procedure described above, in which the calculation of the single term $A(M_0 - 1, M_0)$ is isolated from that of the other $A(N-1, M)$ values, leads to an effective iterative process in which E gradually moves away from the initial unperturbed value towards the required perturbed energy. We found that the calculation of the revised E value could be done between each scan of the indices M and N, without repeating the scan in an attempt to fill up all the $A(N-1, M)$ before evaluating the revised E. Thus the initial value $A(M_0, M_0)$ slowly propagates outwards through the network of $A(N, M)$ values. The sequence of E values produced by this method converges to the perturbed energy directly for sufficiently weak fields. For stronger fields it typically converges to four or more digits, but leads to a sequence with favourable properties for the use of summation techniques. We have used the simple Wynn epsilon algorithm to treat the sequence of E values. For the Stark effect problem, of course, a complex variable form of that algorithm is required; however such a form had already been developed in the previous calculations involving complex hypervirial perturbation theory [8].

In principle the upper limits MU and NU should be gradually increased in order to check for convergence as a function of the basis size. However, it is more simple to find values of MU and NU which are so large that they suffice for all the cases treated. Using such a large dimension also means that the choice of Z becomes less critical.

4. The stark effect calculation

To treat the case of an electric field along the z direction we set $V(1, 1) = \lambda$. We treat the three states $1s_0$, $2p_1$ and $3d_2$, which are not coupled to any other initially degenerate states by the electric field. The value of M_0 is thus 0 for all three states and L is 0,1 or 2. The value of Z is complex, $Z = ZR + iZI$, since we are calculating complex perturbed energies. For small λ values ZR will be close to the value $1/n$ for a state of principal quantum number n. The values found empirically are given in the tables of results. We found that the fixed choice $RA = 0.4$, $RE = 0.2$, $NU = 90$, $MU = 50$ was suitable for all the calculations, allowing around 200 iterations to be performed.

Table 1. Stark effect energies for $L = 0$.

λ	ZR, ZI	ER ($1s_0$)	EI ($1s_0$)
0.002	1.0, 0.02	$-0.500\,009\,000\,889\,0643$	
0.004	1.0, 0.04	$-0.500\,036\,014\,240\,1545$	
0.006	1.0, 0.06	$-0.500\,081\,072\,219\,0729$	
0.008	1.0, 0.08	$-0.500\,144\,228\,820\,0816$	
0.010	1.0, 0.10	$-0.500\,225\,560\,457\,960$	
0.020	1.0, 0.20	$-0.500\,909\,224\,259\,293$	$2.775(-13)$
0.030	1.1, 0.40	$-0.502\,074\,272\,607\,09$	$1.118\,764(-8)$
0.040	1.2, 0.40	$-0.503\,771\,591\,013\,65$	$1.946\,3500(-6)$
0.050	1.2, 0.50	$-0.506\,105\,425\,362\,64$	$3.859\,2083(-5)$
0.060	1.2, 0.60	$-0.509\,203\,450\,8788$	$2.575\,3875(-4)$
0.070	1.3, 0.70	$-0.513\,076\,765\,822$	$9.236\,8428(-4)$
0.080	1.3, 0.80	$-0.517\,560\,617\,006$	$2.269\,8288(-3)$
0.090	1.4, 0.80	$-0.522\,412\,807\,15$	$4.391\,9872(-3)$
0.100	1.5, 0.80	$-0.527\,418\,175\,10$	$7.269\,0568(-3)$
0.120	1.5, 0.80	$-0.537\,335\,5171$	$1.495\,7925(-2)$
0.140	1.5, 0.80	$-0.546\,676\,9462$	$2.462\,9235(-2)$
0.160	1.5, 0.80	$-0.555\,254\,3480$	$3.570\,8138(-2)$
0.180	1.5, 0.80	$-0.563\,054\,517$	$4.779\,442\,29(-2)$
0.200	1.5, 0.80	$-0.570\,124\,900$	$6.061\,4546(-2)$
0.300	1.7, 0.90	$-0.596\,722\,78$	$1.306\,6557(-1)$

In producing the tables of results we proceeded by performing each calculation for gradually increasing field strengths and only went up to field strengths for which at least nine decimal digits of accuracy were obtainable using the fixed set of parameters which we have stated above. For low field strengths (for example for $\lambda < 0.05$ for the $1s$ state) the iterative process converges directly to the complex energy if the complex Z is appropriately adjusted. For larger values of λ the iterated E values converge to between nine and four digits and further digits are obtained by applying a complex variable version of the Wynn epsilon algorithm to the sequences of E values.

Our results for the complex Stark energies of three states are given in tables 1–3. The tables given in [19] set out the results for the $L = 0$ and $L = 1$ cases as obtained by many previous workers using a variety of techniques. The best results for the $L = 0$ case are those of [28] and the best results for the $L = 1$ case are those of [29]. Our results for these two cases are as good as or better than those of [28] and [29] for those values of λ which we have included in our tables. For λ values below 0.01 our results for the $L = 0$ case are in agreement with the very accurate ones given in [14]; for such weak fields neither our method nor that of [14] was able to yield a stable result for the very small imaginary part of the complex eigenvalue. For the $L = 2$ case we could not locate any previous results in the literature and so our results for $L = 2$ are presumably new.

To check the complex energies obtained in our calculations we tested for stability against small variations in the complex Z value and in the two upper limits NU and MU. The stability was usually better than that obtained by previous workers who checked by using perturbation series expansions about two different points [5].

5. The zeeman effect calculation

To represent the perturbation $V = (\gamma^2/8)(x^2 + y^2)$ we set $V(2, 0) = -V(2, 2) = \gamma^2/8$. Such a perturbation links only $\Phi(N, M)$ which differ by 2 in their M value. We relabel the

Table 2. Stark effect energies for $L = 1$.

λ	ZR, ZI	ER ($2p_1$)	EI ($2p_1$)
0.001	0.50, 0.10	$-0.125\,078\,224\,037\,103$	
0.002	0.50, 0.10	$-0.125\,315\,691\,665\,497$	2.15(−15)
0.003	0.50, 0.20	$-0.125\,721\,746\,6701$	8.5938(−10)
0.004	0.50, 0.20	$-0.126\,316\,885\,4266$	4.049\,803(−7)
0.005	0.50, 0.20	$-0.127\,146\,612\,703\,96$	1.307\,642\,72(−5)
0.006	0.50, 0.20	$-0.128\,271\,493\,390$	1.090\,158\,42(−4)
0.007	0.55, 0.25	$-0.129\,679\,053\,085$	4.208\,320\,66(−4)
0.008	0.55, 0.25	$-0.131\,261\,459\,924$	1.036\,240\,53(−3)
0.009	0.55, 0.25	$-0.132\,902\,207\,63$	1.956\,357\,94(−3)
0.010	0.55, 0.25	$-0.134\,524\,488\,77$	3.138\,6539(−3)
0.012	0.55, 0.25	$-0.137\,578\,1092$	6.098\,482(−3)
0.014	0.60, 0.30	$-0.140\,308\,5571$	9.607\,915(−3)
0.016	0.65, 0.35	$-0.142\,721\,5694$	1.347\,4643(−2)
0.018	0.65, 0.35	$-0.144\,849\,9837$	1.758\,1311(−2)
0.020	0.65, 0.35	$-0.146\,729\,380$	2.185\,364(−2)
0.030	0.75, 0.35	$-0.153\,356\,64$	4.442\,363(−2)

Table 3. Stark effect energies for $L = 2$.

λ	ZR, ZI	ER ($3d_2$)	EI ($3d_2$)
0.001	0.33, 0.07	$-0.056\,287\,315\,349$	1.706\,757(−7)
0.002	0.35, 0.15	$-0.059\,065\,562\,39$	7.223\,2324(−4)
0.003	0.40, 0.20	$-0.062\,230\,359\,16$	3.724\,6754(−3)
0.004	0.45, 0.25	$-0.064\,633\,8235$	7.754\,7563(−3)
0.005	0.45, 0.25	$-0.066\,434\,4077$	1.218\,652\,02(−2)
0.006	0.50, 0.25	$-0.067\,796\,251$	1.679\,6022(−2)
0.007	0.55, 0.25	$-0.068\,829\,286$	2.148\,5008(−2)
0.008	0.55, 0.25	$-0.069\,607\,55$	2.620\,426(−2)
0.009	0.60, 0.30	$-0.070\,182\,75$	3.092\,703(−2)
0.010	0.60, 0.30	$-0.070\,592\,38$	3.563\,796(−2)

$A(N, M)$ so that every index M is used (rather than half of them). The change is accomplished very easily, as follows. The scanning rules are retained in the same form as that described in section 3. However, M is scanned in steps of 2, starting from $M = M_0$. When the subroutine generating the terms $T1$ to TE is called, the indices $M, M \pm 2$ in the state indices are replaced by MI and $MI \pm 1$, with $MI = (M_0 + M)/2$. Otherwise the calculation proceeds in the standard manner explained in section 3 (using $RA = RE = 1/2, MU = NU = 100$). The value of Z is real and the calculation was found to yield very accurate Zeeman energies. As Z is gradually increased (for a given γ) the number of converged digits in E also increases, until at and beyond a critical Z value the energy converges to full double precision. The iterations are simply continued until all digits are stable; more than a thousand iterations might be needed. Tables 4–6 show results for five states, with two more digits than are available in the copious 12 digit comparison results given in [21]. The energy values in our tables refer to the Hamiltonian in equation (1) and so omit the linear Zeeman term and also the spin contribution. We note that we used only standard double precision. For the case $\gamma = 1$ for the $1s_0$ state the method of [21] required the use of quadruple precision.

Results with more than three or four accurate digits are necessarily incomplete from a physical point of view, since they do not allow for several small terms in the full Hamiltonian

Table 4. Zeeman effect energies for $L = 0$. $(Z = 1 + 3\gamma + \gamma^2/2)$

γ	$E(1s_o)$
0.05	−0.499 376 706 706 14
0.10	−0.497 526 480 401 09
0.15	−0.494 502 945 778 82
0.20	−0.490 381 565 034 76
0.25	−0.485 247 435 259 98
0.30	−0.479 186 552 901 50
0.35	−0.472 280 764 956 07
0.40	−0.464 605 379 868 22
0.45	−0.456 228 386 357 98
0.50	−0.447 210 538 458 07
0.60	−0.427 462 287 757 19
0.70	−0.405 724 068 429 61
0.80	−0.382 283 393 769 46
0.90	−0.357 369 839 402 28
1.00	−0.331 168 896 733 15

Table 5. Zeeman effect energies for $L = 1$. $(Z = 0.5 + 8\gamma)$

γ	$E(2p_1)$	$E(2p_0)$
0.01	−0.124 701 144 177 38	−0.124 850 415 832 55
0.02	−0.123 817 610 347 53	−0.124 406 465 980 88
0.03	−0.122 384 114 684 73	−0.123 681 330 847 76
0.04	−0.120 447 535 409 29	−0.122 693 709 739 63
0.05	−0.118 058 188 453 78	−0.121 464 837 782 07
0.06	−0.115 264 418 759 56	−0.120 016 268 440 71
0.07	−0.112 110 099 393 19	−0.118 368 549 012 10
0.08	−0.108 633 896 258 71	−0.116 540 574 358 37
0.09	−0.104 869 409 125 06	−0.114 549 364 846 70
0.10	−0.100 845 672 373 34	−0.112 410 078 398 63
0.12	−0.092 117 346 403 71	−0.107 739 398 212 67
0.14	−0.082 611 944 676 57	−0.102 618 226 335 67
0.16	−0.072 453 300 012 51	−0.097 116 798 003 62
0.18	−0.061 737 197 914 85	−0.091 290 610 318 11
0.20	−0.050 539 101 715 10	−0.085 184 041 068 19

Table 6. Zeeman effect energies for $L = 2$. $(Z = 0.33 + 12\gamma)$

γ	$E(3d_2)$	$E(3d_1)$
0.01	−0.054 271 834 028 09	−0.054 678 149 523 27
0.02	−0.050 685 874 396 10	−0.052 253 547 538 39
0.03	−0.045 490 563 101 96	−0.048 661 978 337 93
0.04	−0.039 124 530 270 64	−0.044 213 203 232 78
0.05	−0.031 888 753 731 50	−0.039 120 137 635 24
0.06	−0.023 981 234 765 39	−0.033 527 503 781 57
0.07	−0.015 537 608 899 08	−0.027 536 314 143 57
0.08	−0.006 654 630 636 69	−0.021 219 398 776 46

which could contribute to the energy. The vast majority of published Zeeman effect energies share this defect. However, the large number of digits obtained in our calculation does have a

Table 7. $L = 0$ resonance energies for $V = -\lambda r^P$ with $ZR = 1 + (P - 1)/2$.

λ	P	ZI	ER $(1s_0)$	EI $(1s_0)$
0.02	1	0.3	$-0.530\,663\,983\,531\,828$	$2.7815(-12)$
0.04	1	0.5	$-0.563\,067\,242\,935\,423$	$9.607\,327\,00(-6)$
0.06	1	0.7	$-0.598\,479\,496\,219\,583$	$7.974\,049\,95(-4)$
0.08	1	0.9	$-0.636\,534\,339\,528\,426$	$5.085\,202\,51(-3)$
0.10	1	1.0	$-0.674\,574\,135\,731\,900$	$1.346\,928\,83(-2)$
0.02	2	1.0	$-0.571\,711\,825\,725\,305$	$1.691\,488\,42(-2)$
0.04	2	1.0	$-0.626\,370\,617\,413\,66$	$5.897\,703\,24(-2)$
0.06	2	1.5	$-0.666\,112\,984\,513\,90$	$1.018\,691\,80(-1)$
0.08	2	1.5	$-0.697\,796\,457\,924\,84$	$1.427\,210\,741(-1)$
0.10	2	1.5	$-0.724\,423\,333\,443\,45$	$1.813\,923\,003(-1)$

benefit, since it means that some expectation values can be found to high accuracy by energy differencing. If a very small term such as αU, (with $U = r^{-1}$, r^2 or z^2) is added to the potential then the energy shift produced is $\alpha\langle U\rangle$, where $\langle U\rangle$ is the expectation value of U for the perturbed state being treated. Thus, for example, at $\gamma = 0.3$ we find (for the $1s_0$ state) $\langle r^{-1}\rangle = 1.036\,331$, $\langle r^2\rangle = 2.669\,788$, $\langle x^2\rangle = \langle y^2\rangle = 0.866\,197$, $\langle z^2\rangle = 0.937\,393$. These expectation values differ noticeably from their zero field values and show how the spherically symmetric part of the potential contracts the wavefunction while the rest of the potential gives an anisotropic effect which gives a relative stretching of the wavefunction along the z axis. For small γ values it is easy to check that the energy obtained by using the effective radial potential $(\gamma^2/12)r^2$ gives a very good approximation to the ground-state Zeeman energy, as pointed out long ago [22, 23] (despite the claim made in [24]). The accurate results obtainable by the method of this paper allowed us to extend the earlier radial approximation; a sequence of numerical calculations showed that for the $1s_0$ ground state the Zeeman energy can be obtained with even greater accuracy by adding the term

$$DE = \frac{0.052\,084\gamma^4}{1 + 7.89\gamma^2} \tag{9}$$

to the energy obtained using the effective radial potential (which can be found by the present technique).

For example, at $\gamma = 0.12$ the effective radial potential becomes $0.0012r^2$ and gives the energy $-0.496\,444\,27$ to 8 digits. The correction term of equation (8) when added to this result gives the corrected energy $-0.496\,453\,97$, while the accurate method of this paper gives $-0.496\,453\,98$.

6. Some other perturbations

Although section 5 has described a particularly efficient method of labelling to treat the Zeeman effect, it is, of course, possible to use the original calculation for the Zeeman effect (at the expense of having only half as many μ^M terms available to describe the perturbed wavefunction). To show the flexibility of the simple moment method we have applied it to a range of potentials; we give illustrative results for the $1s_0$ ground state. To treat the complex resonance energies for a perturbation $-\lambda r$ or $-\lambda r^2$ we can keep M fixed at the value 0 (because of the radial symmetry) and so only scan the index N. Table 7 shows some typical results, which are more accurate than those given in [8]. The static Van der Waals potential for a hydrogen atom at a distance of d atomic units from a planar metal surface is equal to $-(1/d^3)(r^2 + z^2)$

Table 8. $L = 0$ state energies for $V = -\lambda(r^2 + z^2)$.

λ	ZR, ZI	ER $(1s_0)$	EI $(1s_0)$
0.002	1.2, 0.5	$-0.508\,283\,888\,078$	$1.518\,250(-6)$
0.004	1.2, 1.0	$-0.517\,393\,189\,32$	$1.631\,6893(-4)$
0.006	1.2, 1.0	$-0.527\,391\,459\,634$	$1.130\,458\,64(-3)$
0.008	1.2, 1.0	$-0.537\,717\,942\,614$	$3.301\,227\,99(-3)$
0.010	1.2, 1.0	$-0.547\,851\,906\,60$	$6.558\,9336(-3)$

Table 9. $L = 0$ energies for $V = \mu r + \lambda z$, with $Z = (1.2, 0.5)$.

μ	λ	ER $(1s_0)$	EI $(1s_0)$
0.002	0.035	$-0.499\,795\,7840$	$7.8221(-8)$
0.004	0.050	$-0.499\,829\,8391$	$1.482\,509(-5)$
0.006	0.061	$-0.499\,880\,6088$	$1.192\,057(-4)$
0.008	0.070	$-0.499\,910\,7312$	$3.780\,262(-4)$
0.010	0.078	$-0.499\,970\,7497$	$8.160\,804(-4)$
0.012	0.085	$-0.499\,870\,0753$	$1.382\,919(-3)$
0.014	0.092	$-0.499\,967\,6374$	$2.157\,087(-3)$
0.016	0.098	$-0.499\,703\,3260$	$2.942\,328(-3)$

Table 10. Stark–Zeeman energies for $L = 0$.

λ	γ	ZR, ZI	ER $(1s_0)$	EI $(1s_0)$
0.04	0.05	1.15, 0.4	$-0.503\,124\,025\,26$	$1.573\,22(-6)$
0.04	0.10	1.30, 0.4	$-0.501\,206\,356\,21$	$9.9573(-7)$
0.04	0.15	1.45, 0.4	$-0.498\,084\,3720$	$4.160(-7)$
0.06	0.05	1.15, 0.6	$-0.508\,510\,427\,450$	$2.366\,378\,73(-4)$
0.06	0.10	1.30, 0.6	$-0.506\,463\,502\,73$	$1.857\,2985(-4)$
0.06	0.15	1.45, 0.6	$-0.503\,150\,111$	$1.286\,17(-4)$
0.08	0.05	1.15, 0.5	$-0.516\,837\,605\,09$	$2.179\,3726(-3)$
0.08	0.10	1.30, 0.5	$-0.514\,690\,9310$	$1.933\,588(-3)$
0.08	0.15	1.45, 0.6	$-0.511\,190\,280$	$1.597\,430(-3)$
0.10	0.05	1.30, 0.7	$-0.526\,711\,107\,35$	$7.104\,987\,26(-3)$
0.10	0.10	1.50, 0.7	$-0.524\,599\,5627$	$6.639\,1709(-3)$
0.10	0.15	1.70, 0.7	$-0.521\,118\,225$	$5.945\,230(-3)$

[25, 26], in the lowest order of approximation in which the atom is far from the surface. Here d is the distance of the nucleus from the surface and r and z are the electronic coordinates with respect to the nucleus. If we take $d = 5$ as a plausible lower limit for the relevant range of d values then we should regard the negative coefficient of the potential as going up to a value of around 0.01. Table 8 shows some typical results for the $1s_0$ ground state, with $\lambda = 1/d^3$. The first-order energy would be $-0.5 - \lambda\langle r^2 + z^2\rangle = -0.5 - 4\lambda$. The simple method of this paper shows that the lowest order approximation actually leads to a complex energy, albeit with a small imaginary part. Table 9 gives results for a calculation in which both radial and full Stark effects are present, with an attempt being made to produce an approximate cancellation between the opposite energy shifts produced by the two perturbations. Table 10 gives some specimen results for the Stark–Zeeman effect with both the electric and magnetic fields along the z direction.

Results were also obtained for the resonances due to the perturbing potential $-\lambda z^2$ and for the Zeeman effect with an imaginary field strength. However we regard the results shown in the tables as being sufficiently plentiful to indicate the wide applicability of the calculational method reported here, since the method is simple enough to be applied directly by readers who are interested in such problems.

7. Conclusion

The specimen results presented here demonstrate that even the most simple moment relation in spherical polar coordinates is capable of producing accurate results for the perturbed hydrogen atom and so provides a further illustration of the complexification procedure which is described in the introduction. We wish to point out how the method might be improved and extended to deal with some special cases. By applying the usual perturbative expansion to the moment recurrence relation, following the route which has been followed by previous work [10–12] we arrive at the perturbative form of the method described here. However, we can now produce a dual calculation, with the direct method described in the present work giving a calibratory control over the perturbative results which arise from the same equations. Such a dual calculation has now been carried out for the Zeeman effect and the details will be reported in a work which is currently in preparation. Were such a dual approach to be carried out for the Stark effect then it would lead directly to a complex series, whereas the previous tradition has been to use analytic continuation or other techniques to extract the imaginary part of the energy from the conventional real perturbative series for the energy [5, 27, 28].

We emphasize that the principal aim of the present work is to make the simple method described here available to other workers. An appropriate computer program can be written by any reader in a few hours, since iterative use of just a few equations is all that is required. The tables of numerical results were given in order to demonstrate that the effort of adopting the method would be worthwhile. As is usual for a new technique, we have tested the method on a family of non-degenerate states, for which the simple initial condition $A(M_0, M_0) = 1$ will suffice. When it comes to the Stark effect for the $2p_0$ state, however, two or more $A(M, N)$ will need to be fixed, with a ratio which will have to be determined to pick out one of the two partner states which arise from the coupling of that state with the $2s_0$ state. This problem also arises in the perturbation theoretic version of the theory and has been given an elegant solution by Fernandez [10]; accordingly, we conjecture that a similar approach will provide a solution to the same problem of degeneracy in our direct secular equation use of the moment equations.

The algorithm of the present work has been presented in this context of moment theory, since that is the form previously adopted by workers who have taken an approach based on perturbation theory. It thus facilitates the kind of dual purpose (iterative/perturbative) calculations mentioned previously. However, as noted in section 2, we have used a set of basis functions which are essentially complete for the problems being considered. Our approach can thus be regarded as equivalent to a type of Hill determinant approach in two dimensions, which would make it a more complicated version of the Hill-series approach already used for resonances in one dimension [9]. The complexification approach proceeds by taking initial formulae which work for bound states (and thus involve real wavefunctions) and then giving complex values to either a nuclear charge or an oscillator frequency, while retaining the original form of the equations for the bound state theory. This approach sidesteps the explicit task of studying the modified form of inner product which is implicit in the formation of matrix elements for the study of resonance states, although previous work indicates that it is appropriate to suppress the usual complex conjugation operation on one term when making

an explicit matrix calculation for such states [7]. In terms of matrix iterative methods our calculation is essentially a modified Gauss–Seidel approach to finding the lowest eigenvalue of a very large matrix in which each element is complex and is also specified by two indices. The explicit algebraic expressions for the matrix elements make it possible to perform the task without the actual construction of the enormous matrix which is implicit in the calculation.

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