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# The exponential cosine screened potential

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**Abstract.** The concept of forwards-nested multiplication is used to develop a unified power series–Hill determinant method for the calculation of Schrödinger-equation energy levels. A numerical application is made to the exponential cosine screened potential.

## 1. Introduction

Some particular forms of the radial Schrödinger equation

$$-\alpha D^2\psi - Zr^{-1}U(r)\psi = E\psi \quad (1)$$

with  $U(r) = \exp(-\mu r) \cos \lambda r$  have been the subject of many numerical calculations. The Yukawa potential, with  $\lambda = 0$ ,  $\mu > 0$ , has been treated by Rayleigh–Schrödinger theory and Padé approximants (Lai 1981, Vrscay 1986), by a scaling-variational approach (Gerry and Laub 1985), by a  $Z^{-1}$  expansion method (Iafate and Mendelsohn 1969) and by the Ecker–Weizel approximation (Dutt *et al* 1981). The exponential cosine screened Coulomb potential, with  $\lambda = \mu > 0$ , has been treated by perturbation theory with  $\lambda$  as the perturbation parameter (Lai 1982, Ray and Ray 1981), by perturbation theory based on the Hulthén potential (Lam and Varshni 1972, Bessis *et al* 1975), by an algebraic perturbation method (Roychoudhury and Roy 1985) and by the Ecker–Weizel approximation (Ray and Ray 1980). The case  $\lambda \neq \mu$  was treated by Fack *et al* (1986) using an algebraic perturbation method.

The present work sets out a very simple dual-purpose method for calculating the energy eigenvalues of equation (1); the calculation can be used either in a Hill determinant mode (with the boundary conditions  $\psi(0) = \psi(\infty) = 0$ ) or in a power series mode with  $\psi(0) = \psi(L) = 0$  for some finite  $L$ ). Section 2 sets out the basic equations of the method. Section 3 discusses the link between the power series and Hill determinant approaches to eigenvalue calculation and § 4 presents some typical numerical results. Section 5 comments on further applications of the methods described in this work.

## 2. The basic recurrence relations

A key feature which makes the calculations of this work tractable on a microcomputer is the fact that both the potential and the wavefunction have rapidly convergent power series expansions with coefficients which obey a recurrence relation. The function  $U(r) = \exp(-\mu r) \cos \lambda r$  may quickly be shown to obey the differential equation

$$U'' + 2\mu U' + (\mu^2 + \lambda^2)U = 0. \quad (2)$$

If we construct the power series solution

$$U = \sum_0^{\infty} U(m)K^{-m}r^m \quad (3)$$

where  $K$  is a numerical scaling factor (for computational convenience) we find by inspection that  $U(0) = 1$ ,  $U(1) = -\mu K$  and that the rest of the  $U(m)$  follow from the recurrence relation

$$(m+1)(m+2)U(m+2) + 2\mu(m+1)KU(m+1) + K^2(\mu^2 + \lambda^2)U(m) = 0. \quad (4)$$

Thus the power series expansion of the potential in the Schrödinger equation (1) can be computed rapidly to a large number of terms.

We now study the regular series solutions of a radial Schrödinger equation in which the potential is represented by a convergent power series

$$-\alpha D^2\psi + \sum_{-1}^{\infty} V(m)r^m\psi + \alpha l(l+1)r^{-2}\psi = E\psi. \quad (5)$$

Equation (5) is usually thought of as being the equation for the radial wavefunctions associated with states of angular momentum  $l$  in three dimensions. However, equation (5) and hence the methods of this work can also be applied to states of generalised angular momentum  $\Lambda$  in  $N$  dimensions; all that is required is to use the numerical value  $l = \frac{1}{2}(2\Lambda + N - 3)$  in the  $r^{-2}$  term of equation (5) (Killingbeck 1985a).

The regular solution for equation (5) is postulated to take the form

$$\psi = \exp(-\beta r) \sum_0^{\infty} A(n)r^{n+l+1} \quad (6)$$

where  $\beta > 0$  is an adjustable convergence parameter.

From equations (1), (3) and (5) we can see that the relation

$$V(m) = -ZU(m+1)K^{-(m+1)} \quad (7)$$

holds. To simplify the equations and computations we introduce the definition

$$A(n) = B(n)K^{-n}. \quad (8)$$

When (6) is substituted into (5) we finally obtain the recurrence relation

$$(n+2l+3)(n+2)B(n+2) - 2\beta K(n+l+2)B(n+1) + K^2(\beta^2 + E\alpha^{-1})B(n) - \alpha^{-1}ZK \sum_{-1}^n U(m+1)B(n-m) = 0. \quad (9)$$

For a given trial  $E$  we use the initial conditions  $B(n) = 0$  for  $n < 0$ , together with an arbitrary  $B(0)$  value, to compute the  $B(n)$  for  $n > 0$ . The  $A(n)$  usually fall off rapidly at high  $n$ , but the  $B(n)$  do not fall off so rapidly if  $K$  is given a value greater than unity; the value  $K = 4$  has been used for most of the calculations carried out so far by the methods reported here. Similarly, the presence of  $K$  in equation (7) produces non-zero  $U(m)$  values at high  $m$ , where the original  $V(m)$  would be below the microcomputer underflow level.

### 3. The Hill determinant and power series approaches

The procedure which makes it possible to include both a Hill determinant and a power series calculation in one uniform algorithm is the forwards-nested multiplication

procedure devised by Killingbeck (1985b). The traditional nested-multiplication algorithm attacks the problem of evaluating a sum of form

$$\psi(x) = \sum_0^N A(n)x^n \quad (10)$$

by starting from the top end (i.e.  $n = N$ ) and using the steps

$$S(0) = A(N) \quad (11)$$

$$S(n+1) = xS(n) + A(N-1-n) \quad n \geq 0 \quad (12)$$

with

$$\psi(x) = S(N+1). \quad (13)$$

However, we usually compute power series with the *lower*  $A(n)$  taken first. To find the effect of adding an extra term  $A(N+1)x^{N+1}$  using the traditional algorithm involves starting at the top and working down again. If, however, we rewrite (10) in the form

$$\psi(x) = x^N \sum_0^N A(N-n)y^n = x^N F(N) \quad (14)$$

with  $y = x^{-1}$ , then the algorithm to compute the factor  $F(N)$  clearly takes the form

$$F(0) = A(0) \quad (15)$$

$$F(n+1) = yF(n) + A(n+1) \quad n \geq 0 \quad (16)$$

which permits an easy calculation of the effect of adding one more term to the series. In the present work a further simplification results; we wish to compute only the ratios of two  $\psi(x)$  values, with  $N$  and  $x$  the same for both but with different coefficients  $A(n)$ . This means that the factor  $x^N$  in (14) can be omitted, so that the sum  $F(N)$  is all that needs to be calculated to represent  $\psi(x)$ .

The method of calculation in the power series approach (Secrest *et al* 1962, Killingbeck 1981) is to assign a trial  $E$  value and to sum the power series for the wavefunction  $\psi(x)$  at a fixed  $x$  value,  $x = L$ , varying  $E$  to search for a zero of  $\psi(L)$ . The resulting  $E$  values are eigenvalues appropriate to the Dirichlet boundary condition  $\psi(L) = 0$ . The preceding discussion shows that if we use a fixed large number  $N$  of terms of the series then we can represent  $\psi(L)$  by a sum which is computed using the recurrence relation (16), so that  $y = L^{-1}$  becomes the relevant spatial variable. To compute eigenvalues in the limit  $L \rightarrow \infty$  we set  $y = 0$  in (16), which then shows that the quantity to be studied and rendered zero as a function of  $E$  is the coefficient  $A(N)$  alone rather than the sum of the series. Ginsburg (1982) noted empirically that a 'zero coefficient' test served to produce eigenvalues for power series potentials and Kok (1987) used it for a Yukawa potential with very small  $\mu$  ( $\mu < 0.01$ ). Killingbeck (1985a) showed that the zero coefficient test is equivalent to the use of the Hill determinant approach. The arguments presented in the present work thus show that the Hill determinant method can be regarded as arising naturally within the formalism of the power series method. The relationship between the Hill determinant method and the inner product method for eigenvalue calculation is discussed by Killingbeck (1987a).

#### 4. Some specimen results

The numerical calculations are carried out using a combination of the ideas of §§ 2 and 3. The recurrence relation (4) is used to compute a large number of the coefficients

$U(n)$  which represent the potential for the specified  $\mu$  and  $\lambda$  values. Then, for a specified  $x$  value  $x = L$ , the recurrence relation (9) is used (typically with  $B(0) = 10^{30}$ ) to compute the  $B(n)$  up to the value  $n = N$  for some fixed large integer  $N$  (typically ranging from 20 up to 60) and some trial  $E$  value. The quantities  $F(n)$  are simultaneously calculated using the initial value  $F(0) = B(0)$  and the recurrence relation

$$F(n+1) = (K/L)F(n) + B(n+1) \quad (17)$$

which is the appropriate version of (16) when we allow for the scaling factor  $K$  in the definitions. The trial energy  $E + \Delta$  (with  $\Delta$  typically  $10^{-3}$ ) is next used, giving a different  $F(N)$ . From the two  $F(N)$  values a linear extrapolation gives an estimated energy  $EP$  which would have made  $F(N)$  zero.  $EP$  then becomes the new  $E$  estimate for the next cycle of the process, until the  $E$  value has converged. The computational procedure is essentially a finite difference simulation of Newton's method which avoids explicit differentiation (Killingbeck 1985b). To obtain the Hill determinant results the calculation is performed with  $L$  set at a very large value (e.g.  $L = 10^{20}$ ) so that  $F$  and  $B$  become equivalent in (17). At each  $N$  value (and for fixed  $L$  and  $l$ ) a sequence of eigenvalues results. As  $N$  is increased the lower eigenvalues stabilise to limiting values which can be taken as the eigenvalues for the Schrödinger equation. We checked a selection of results for a variety of  $\mu$  and  $\lambda$  values in the references cited in § 1 and obtained good agreement (or improvement). We regard our results as accurate to the number of digits quoted. The results in table 1 for  $\lambda = \mu = 0.05$  differ in the last few digits from those of de Meyer *et al* (1985) and of Roy and Choudhury (1985). The agreement between the results of those two earlier approximate calculations arises because both works involved neglect of the same off-diagonal matrix elements, as indicated by de Meyer *et al* (1985). For the results displayed in tables 1-3 we should note that only about twenty terms of the power series for the potential (actually the  $U$  coefficients) registered as non-zero on the microcomputer employed. Deleting the last few non-zero coefficients makes a negligible change in the eigenvalues, indicating that the coefficients used are sufficient to represent the potential function correctly; this favourable circumstance is presumably brought about by the rapid convergence of the power series for both the potential and the wavefunction. For very weakly bound states, with  $E$  just below zero, the value of  $N$  required to obtain full convergence of the energy may rise to around 100; however, numerical experiments showed that good estimates of  $E$  can be found by simple Aitken extrapolation based on three successive  $E$  values (e.g., at  $N = 50, 55, 60$ ), thus cutting down on the required

**Table 1.** Some results for  $\alpha = \frac{1}{2}$ ,  $Z = 1$ , showing the  $N$  value required for convergence (as judged by comparing results at  $N$  and  $N + 5$ ).  $\beta = 1$  throughout.

$N$	State	$(\mu, \lambda)$		
		(0.05, 0)	(0, 0.05)	(0.05, 0.05)
20	1s	-0.451 816 43	-0.498 129 26	-0.450 117 47
40	2s	-0.081 771 20	-0.117 675 77	-0.076 449 60
40	2p	-0.080 740 39	-0.118 887 67	-0.076 059 01
60	3s	-0.019 352 55	-0.040 204 57	-0.011 575 56
60	3p	-0.018 557 75	-0.041 310 45	-0.010 929 34
60	3d	-0.016 915 57	-0.043 451 21	-0.009 554 89
	dp/ps	2.066	1.936	2.127

computing time and on rounding errors. Table 1 shows some specimen results for the six lowest energy levels.

In the theory of atomic energy levels (Condon and Shortley 1953) the energies  $E(J)$  in an  $LSJ$  multiplet with weak spin-orbit coupling are proportional to  $J(J+1)$ , so that the energy gap  $E(2) - E(1)$  is twice as large as the energy gap  $E(1) - E(0)$ . This well known interval rule of atomic spectroscopy has an analogue in the results of table 1. The energy gap ratio for the states with  $n=3$  obeys the interval rule  $dp/ps > 2$ , but for the case  $\mu = 0$ ,  $\lambda = 0.05$  the order of the levels is inverted. At first sight it might seem that for small splittings a first-order theory with  $\alpha l(l+1)r^{-2}$  regarded as a perturbation would explain the interval rule. However, such a positive-definite perturbation would not give an inverted level order. Table 2 shows some results which we obtained by exploiting the fact that  $l$  does not have to be an integer in the algorithms of this paper. The results show that the 2p energy arises from the 1s energy (not the 2s energy) as  $l$  varies from 0 to 1, so it is incorrect to regard the 2p energy as derivable from the 2s energy by using the centrifugal potential as a perturbation. Similarly we have the correlations  $1s \rightarrow 3d$ ,  $2s \rightarrow 3p$ , which lead to similar conclusions for the  $n=3$  levels. The correct explanation of the interval rule seems to us to arise from the fact that the hydrogenic degeneracy is being broken by a potential which (for small  $\mu$  and  $\lambda$ ) is dominated by the  $r^0$ ,  $r$  and  $r^2$  terms. Both  $\langle r \rangle$  and  $\langle r^2 \rangle$  for hydrogenic orbitals equal  $l$ -independent terms plus a term proportional to  $l(l+1)$  (Condon and Shortley 1953), so that the interval rule still holds for small splittings but the *sign* of the splittings depends on the coefficients of  $r$  and  $r^2$  in the potential.

**Table 2.** Energy eigenvalues as a function of  $l$ , showing the evolution of the 2p energy from the 1s energy.  $N = 50$ ,  $\beta = 1$  and  $L = 10^{20}$  throughout.

$l$	$(\mu, \lambda)$		
	(0, 0)	(0, 0.05)	(0.05, 0)
0.0	-0.500 000 00	-0.498 129 26	-0.451 816 43
0.2	-0.347 222 22	-0.344 682 68	-0.299 669 44
0.4	-0.255 102 04	-0.251 799 65	-0.208 260 77
0.6	-0.195 312 50	-0.191 156 88	-0.149 259 66
0.8	-0.154 320 99	-0.149 226 66	-0.109 129 83
1.0	-0.125 000 00	-0.118 887 67	-0.080 740 39
$E(2s)$	-0.125 000 00	-0.117 675 77	-0.081 771 20

Table 3 illustrates how the method of this work can be used to show the dependence of energy levels on the value of the bounding coordinate  $L$ . Clearly the spatially more compact ground state reaches its limiting energy more quickly than do the excited states. Table 4 shows some specimen results for the 3s state which show that (for this case) the 3s eigenfunction must have nodes at  $x \sim 6.88$  and  $x \sim 1.88$ , since at these  $L$  values the Dirichlet problem gives an energy level at the same energy as that of the 3s state for the limit  $L \rightarrow \infty$ . We note that each *individual* energy level falls monotonically as  $L$  increases, but in the critical regions shown in table 4 *different* states have energies passing through the particular  $E(3s)$  value. For example, close to  $L = 1.88$  the lowest level for the boundary condition  $\psi(L) = 0$  agrees with the third level for the boundary condition  $\psi(\infty) = 0$ . A more direct way to find the node positions is to find  $E(3s)$ , hold  $E$  fixed at that value, and then compute  $F(N)$  for some large  $N$  and with  $x$

**Table 3.** Variation of energy with  $L$  for the case  $\alpha = \frac{1}{2}$ ,  $Z = 1$ ,  $\mu = 0$ ,  $\lambda = 0.05$ .  $\beta = 1$  and  $N = 50$  throughout.

$L$	State		
	1s	2s	2p
10	-0.451 815 62	-0.068 550 64	-0.073 903 65
15	-0.451 816 43	-0.081 126 75	-0.080 429 25
20	-0.451 816 43	-0.081 749 44	-0.080 730 50
$10^{20}$	-0.451 816 43	-0.081 771 20	-0.080 740 39

**Table 4.** Typical results to indicate node positions for the 3s state with  $\alpha = \frac{1}{2}$ ,  $Z = 1$ ,  $\mu = 0$ ,  $\lambda = 0.05$ .  $\beta = 1$  and  $N = 50$  throughout.

$L$	$E$	Level
$10^{20}$	-0.040 204 57	3rd
7.00	-0.046 494 11	2nd
6.90	-0.041 887 27	2nd
6.80	-0.036 968 55	2nd
1.90	-0.053 024 56	1st
1.89	-0.045 133 96	1st
1.88	-0.037 083 86	1st

being gradually increased; a sign change in  $F(N)$  then indicates that  $x$  has passed through a node in the eigenfunction. The value of the parameter  $\beta$  was not found to be too crucial; for the results reported here any value between roughly 0.2 and 1.5 gave reasonable convergence in  $N$ .

## 5. Further applications

The methods described in this work can easily be adapted to deal with any radial potential with a rapidly converging power series which satisfies a differential equation; the potential  $-A \exp(-\lambda r^2)$  discussed by Lai (1983) falls into this category. The method can obviously be applied to problems for which the potential is a finite polynomial; e.g., the confined oscillator problems which Fernandez and Castro (1981) treated using a hypervirial technique. Killingbeck (1987b) has recently developed a shooting-relaxation method to calculate the Zeeman energy levels for a Coulomb potential; that method in principle will work for any radial power series potential and so should permit the calculation of Zeeman energy levels for the family of potentials studied in the present work. The phenomenon of 'false' eigenvalues (Killingbeck 1986) can be demonstrated for the calculations of this work; for example, the use of the value  $\beta = -1$  instead of  $\beta = 1$  in the reported calculations leads to different energies. These are actually energies for a partner potential in which the sign is reversed for the odd powers of  $r$  in the power series; for this case the partner potential is  $Zr^{-1} \exp(\mu r) \cos(\lambda r)$ . Although energy levels are displayed in the present paper, the calculation of expectation values such as  $\langle r^n \rangle$  can be carried out using the techniques developed by Killingbeck (1985c).

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