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J P Killingbeck†, T Scott† and B Rath‡

† Department of Mathematics, University of Hull, Hull HU6 7RX, UK
‡ Department of Physics, Ravenshaw College, Cuttack 753001, India

Abstract. Several useful techniques are described for treating power series potentials. These include: a moving row matrix nested multiplication method for constructing the Hamiltonian matrix; a scaled folding algorithm to find the eigenvalues; and an energy shift method which gives expectation values and eigencolumn elements. Two test problems are treated using the techniques; in particular, it is found to be possible to treat a triple-well problem using only a simple single-oscillator basis set.

In this paper, we describe several useful techniques which facilitate the use of the matrix diagonalization approach to the Schrödinger equation for the case of a power series potential. To the best of our knowledge, some of these techniques do not appear to have been reported in the current literature on the subject. Applications to a single- and to a triple-well potential produce several interesting results which can be reasonably well explained by the use of arguments based on physical intuition. It is our intention not just to present some numerical results, but also to set out the novel and useful features of the techniques in sufficient detail to make them applicable by the many physicists who use matrix methods in their work. Accordingly, we have set out in detail some of the vital steps which render the calculations efficient.

1. Hamiltonian matrix construction

In a matrix diagonalization approach to the calculation of energy levels for the Schrödinger equation, the first essential step is the calculation of the Hamiltonian matrix. If the basis states used are the eigenfunctions of the harmonic oscillator Schrödinger equation

$$H_0\psi = -\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \beta^2 x^2 \psi = E\psi \tag{1}$$

then in principle, the matrix elements of x^N are known analytically, but involve many square root expressions for moderately high N values. As pointed out in [1], symbolic languages such as MAPLE can produce the relevant formulae; nevertheless, a numerical substitution is needed to obtain the actual matrix elements. In this work we stress the value of a direct numerical construction of the matrix *in situ* by using matrix nested multiplication for the *full* polynomial potential. Previous authors [1–3] have used matrix multiplication for the (slower) evaluation of each individual x^N term in the potential; [1] found that this approach is more reliable numerically than the use of the explicit summation formulae of [4] for the x^N matrix elements.

Besides applying full matrix nested multiplication, this paper also explains clearly how to overcome the important 'edge effect' (which is not mentioned by the cited works) and how to find polynomial expectation values without the need for knowledge of any eigencolumns. It also shows that it is even possible to find individual normed eigencolumn elements by a procedure which uses only eigenvalue calculations.

We assume that the Schrödinger equation involves the Hamiltonian

$$H = H_0 + \sum_{K=0}^{M} V(K) x^{2K} \tag{2}$$

where H_0 is the harmonic oscillator Hamiltonian in equation (1). We note that, in general, the x^2 term in the potential will need to be appropriately partitioned between H_0 and the perturbing potential if the potential is held fixed while the value of β^2 in the basis set is varied. With the potential written in the form appearing in equation (2), the matrix elements of H_0 are the traditional diagonal ones, namely

$$H_0(J, J) = (2N(J) + 1)\,\beta \tag{3}$$

where we introduce the indexing formula

$$N(J) = 2J + P - 2 \tag{4}$$

to map the matrix index J to the H_0 state quantum number $N(J)$. The parity index P is 0 for even states and 1 for odd states. The diagonal matrix elements of H_0 are added to the H matrix *after* the matrix of the perturbing potential has been calculated by a matrix nested multiplication procedure in which the matrix is built up step by step according to the rule

$$H(I + 1) = H(I) * X2 + V(M - I) * \boldsymbol{I} \qquad (I = 0, \ldots, M) \tag{5}$$

where $H(0)$ is the $N \times N$ null matrix, $\boldsymbol{I}$ the $N \times N$ unit matrix and $X2$ the tridiagonal matrix of x^2 (with elements given below). In applying equation (5) the detailed assignment statement which gives the new elements at the first matrix multiplication stage

$$H := H * X2$$

is (with the usual convention of new values on the left, old values on the right)

$$H(J, K) := H(J, K) * A + H(J, K + 1) * B + H(J, K - 1) * C \tag{6}$$

where A, B and C are the standard oscillator matrix elements

$$\begin{aligned}
A &= (2\beta)^{-1}\,(2N(K) + 1) \\
B &= (2\beta)^{-1}\sqrt{(N(K) + 2)\,(N(K) + 1)} \\
C &= (2\beta)^{-1}\sqrt{N(K)\,(N(K) - 1)}
\end{aligned} \tag{7}$$

and $N(K)$ is found by using the indexing formula of equation (4).

Inspection of equation (7) shows that the calculation of some of the matrix elements of the $N \times N$ matrix $H(I + 1)$ will require knowledge of elements of $H(I)$ which are outside the $N \times N$ matrix. Concentrating strictly on only the 'inner' elements during the nested multiplication will thus give an 'edge effect' which produces incorrect matrix elements in a rim around the sides of the H matrix. To remove this error the matrix is worked out one row at a time, with the elements being held in a single temporary storage row T, so that $H(J, K)$ is put in the $T(K)$ element. The row T can then be very long—quite sufficient to carry out an exact calculation with K going well beyond the required matrix dimension N. The elements

$T(K)$ up to $K = N$ are then copied into the row J of the H matrix and the working row T is set to zero ready for the calculation of row $J + 1$. This row-by-row approach also has the advantage that it is suitable for use with iterative matrix algorithms, e.g. [5], which compute eigenvalues by using only one row at a time with repeated computation of the desired elements.

As is clear from equation (6), only the matrix elements of x^2 are explicitly stated during the calculation. For a potential with a rapidly converging power series, the above procedure gives (except for rounding errors) the correct Hamiltonian matrix. The HEG method [6–8] would treat the problem by first diagonalizing the x^2 matrix in the oscillator basis and then approximating the matrix of $V(x^2)$ by substituting $V(x_j^2)$ at the diagonal position occupied by the eigenvalue x_j^2. This procedure leads to errors in the matrix which are difficult to quantify. It also of course involves a preliminary diagonalizing transformation for the x^2 matrix together with a simultaneous transformation of the kinetic energy matrix, which is non-diagonal in the oscillator basis. This paper gives some specimen calculations which indicate that the direct route described here is effective for potentials comprising rapidly converging power series. The calculation of the H matrix can clearly be carried out by a computer program which mainly involves the repetition of appropriate loops. The initial V coefficients can be given as data or can be produced by a separate subroutine which generates the power series V coefficients for the required potential. We give results for one problem in each of these categories.

2. Scaled folding algorithm

It is clear that once the H matrix has been formed, the task of finding the eigenvalues and eigencolumns can be carried out by any standard matrix technique. For the well spaced eigenvalues of our test problems, it is sufficient to use the simple folding algorithm of [9], which is essentially a Gaussian elimination method for working out the determinant $DET(E) = det(H - E\boldsymbol{I})$ and varying E to find the zeros of the determinant. The folding algorithm has as its principal element the repetition of the 'folding' operation which can be described by the assignment statements

$$C(J, K) := C(J, K) - C(J, M)C(M, K)/C(M, M) \tag{8}$$

$$DET := DET \times C(M - 1, M - 1). \tag{9}$$

Here C is the 'copy' matrix formed by copying H into C and then subtracting E times the unit matrix. At each step the $(M - 1) \times (M - 1)$ submatrix of C is overwritten according to equation (8), as the index M is reduced from N down to 2. DET is initialized to $C(N, N)$ and is modified at each step by means of equation (9), reaching a final value which is the determinant of $H - E\boldsymbol{I}$. A root-finding subroutine can be combined with this calculation to find the matrix eigenvalues as the zeros of $DET(E)$. If required, the eigencolumns can be obtained by inverse iteration using a modification of the folding algorithm which includes two columns X and Y and solves the equation system $Y = (H - E\boldsymbol{I})X$ for X [9]. Although we did calculate some eigencolumns (as reported below), we were also able to obtain much useful information by using the eigenvalue perturbation technique described below.

One of the technical steps which we found necessary in using the folding algorithm is of general value and so is briefly described here. For large matrices and for trial E values which are far from an eigenvalue, the value of the product DET can become extremely large, causing overflow problems during the computation. This difficulty is avoided by setting up a row $CS(J)$ which stores the computed $C(J, J)$ on the *first* folding calculation and then uses the normalized value $C(M - 1, M - 1)/CS(M - 1)$ in the DET product of equation (9), but *not* in equation (8). In particular, this scaling is done on the *first* run itself so that the initial value of DET is effectively normalized to 1.

We found that this procedure is adequate to keep the *DET* values within a moderate numerical range as the trial *E* varies in the search for the zeros of *DET*. The interesting feature emerged that this simple scaling of the factors in *DET* sufficed, without a more complicated scaling of all the elements $C(J, K)$ which appear in the intermediate stages of the C matrix as it is gradually modified by the folding process. The folding algorithm has the advantage of leaving unchanged the bandwidth of a matrix and hence is particularly rapid for matrices of limited bandwidth, such as those associated with the second calculation reported in this work.

The first potential for which we show specimen results is the Gaussian potential

$$V = -100e^{-x^2} \tag{10}$$

which is represented by an alternating series in x^2. Previous authors [2, 3] have given closed expressions for the relevant matrix elements or lozenge-type recurrence relations for their computation, but here we test the direct nested multiplication approach based on the coefficients $V(J)$ of the exponential series. Our purpose is twofold, to test the technique and to exploit the traditional bounding properties of alternating series.

Various considerations of a physical nature help to guide the computation and to interpret the results. It is intuitively clear that the truncated series used is only required to give an accurate representation of the potential function in the region where the wavefunction is of appreciable magnitude for the particular state being considered. Also, if the number of terms taken is always even, the actual potential used always has a discrete spectrum and provides an upper bound to the true Gaussian potential. Since the eigenvalues of the H matrix are themselves upper bounds to the exact bound state eigenvalues, it follows that we have a calculation which must give upper bounds to the exact eigenvalues. In principle, there are three parameters which should be varied: M, the upper index in the potential appearing in equation (2); N, the dimension of the matrix (i.e. the number of basis states); and β^2. However, it is possible to do a short preliminary calculation and decide on values of β^2 and N which suffice to give converged results in N for all the states to be treated.

For the Gaussian potential the higher states have rapidly increasing spatial extent. We have therefore used a compromise β^2 value of 40, rather than the value $\beta^2 = 100$, which at first sight appears appropriate for the very lowest states (since $V = -100 + 100x^2 - \cdots$). With fixed β^2 and N, the calculation can then concentrate on studying the effect of increasing M.

Table 1 shows results for the lowest five levels of the Gaussian test potential. Table 2 displays the rate at which the upper bound descends to the exact eigenvalue as M is increased for one eigenstate. Also shown are the results for odd M values, which give a sequence of lower bounds to the energy. At first sight this lower bound property seems obvious, since the sum of an odd number of terms gives a lower bound to the true potential. However, the series actually represents a potential which ultimately diverges to $-\infty$ and hence, in principle, has very narrow resonances rather than true bound states. For such a potential our calculation should strictly

Table 1. Energy levels for the potential $V = -100e^{-x^2}$ with $\beta^2 = 40$ and $N = 60$. The M value shown is that required to give the displayed energy. The $\langle x^2 \rangle$ are also shown, along with β_0^2, the effective value of β^2 which corresponds to the actual $\langle x^2 \rangle$ value for each state.

E	M	$\langle x^2 \rangle$	β_0^2
$-90.376\,398\,798\,077$	16	0.0541	85
$-71.916\,893\,344\,509$	20	0.1727	75
$-55.080\,167\,079\,855$	24	0.3160	63
$-39.974\,972\,170\,785$	32	0.4959	50
$-26.746\,369\,362\,935$	46	0.7346	38

Table 2. The third energy level for $V = -100e^{-x^2}$ as a function of M, with $\beta^2 = 40$ and $N = 60$. All results start with the initial part $-55.080\,16$ and only the next varying seven digits are shown in the table.

M	E	M	E
12	6231 758	13	7294 584
14	7028 774	15	7089 642
16	7076 167	17	7081 319
18	7079 539	19	7079 966
20	7079 824	21	7079 866
22	7079 852	23	7079 857
24	7079 855		

speaking be regarded as a stabilization calculation in the spirit of the work by Hazi and Taylor on resonance states [10]. It turns out, however, that the calculation is appropriate for this case, since, before the potential represented by the truncated series descends, it reaches a maximum which is so high compared with the eigenvalue studied that the tunnelling effects are virtually negligible.

3. Energy shift method

In this case we obtain well converged results at a dimension $N = 60$, but as would be expected, we find that higher states with larger spatial extent need more terms in the V series to represent the true potential. The value of $\langle x^{2K} \rangle$ for $K = 1, 2, \ldots$ can be found by a simple method which does not require the use of the eigencolumn and the matrix of x^2. The eigenvalue is recomputed with $V(K)$ increased by a very small increment α; the energy change is then $\alpha \langle x^{2K} \rangle$ to first order of perturbation theory. By using a few α values together with Richardson extrapolation, this approach can be refined to give $\langle x^{2K} \rangle$ to very high accuracy, but even the simple 'single shift' method gives satisfactory estimates that reveal the extent to which the wavefunctions expand as the energy increases. It also provides a useful diagnostic tool for the interpretation of the results of our second calculation.

This second calculation is the most interesting one selected from a set of triple-well potential calculations. The sequence of even-parity potentials of the form

$$V = x^6 - 20x^4 + Ux^2 \tag{11}$$

exhibit three potential wells. For $U = 100$ the three wells all have their minimum at $V = 0$. For $U = 110$ the outer wells have a minimum which is at about $V = 97$, while for $U = 90$ the outer wells have their minimum at about $V = -102$. For the case $U = 90$ which we study, conventional wisdom might indicate that it is necessary to use a distributed basis set which allocates a set of oscillator functions to each well to ensure a sufficiently rich set of basis functions to describe those regions where on physical grounds we expect the wavefunction to be large. Some authors [11, 12] use such an approach, which involves the use of non-orthogonal basis functions. However, for a simple double-well potential it has been observed that a single-oscillator basis centred on $x = 0$ can be chosen to give accurate double-well levels [13, 14].

In table 3 we show results for the potential given in equation (10) with $U = 90$ and using an oscillator basis which appears to be appropriate to describe only the levels in the central well, i.e. with $\beta^2 = 90$. As the dimension N is increased, the levels do at first appear to tend towards such levels, with $E > 0$. However, as N is increased further through this region of

Table 3. Energies and $\langle x^2 \rangle$ values for low-lying states of the potential $V = x^6 - 20x^4 + 90x^2$ with $\beta^2 = 90$ and $N = 80$. The centre of the deep outer pair of wells is at $x^2 \approx 10.47$. The parity even, odd means that the even–odd splitting is too small to show up at this level of precision.

E	$\langle x^2 \rangle$	Parity
$-80.858\,181\,599\,472$	10.29	even, odd
$-39.293\,336\,763\,202$	9.91	even, odd
$-0.083\,416\,049\,69$	9.48	even, odd
$9.315\,165\,356\,793$	0.055	even
$27.583\,821\,595\,213$	0.169	odd
$36.438\,171\,475\,228$	8.99	even
$36.438\,171\,475\,404$	8.99	odd
$45.093\,481\,756\,703$	0.294	even
$61.760\,180\,906\,442$	0.434	odd
$69.742\,235\,886\,435$	8.37	even
$69.742\,242\,087\,840$	8.37	odd

'quasi-convergence', the correct spectrum of levels emerges, including the levels for which the wavefunction is almost entirely concentrated in the outer wells and for which $E < 0$. Here again we can invoke physical intuition to understand this apparently astonishing phenomenon.

The value of $\langle x^2 \rangle$ for an oscillator function with quantum number n is $(n + \frac{1}{2})\beta$. The matrix diagonalization is essentially trying to form a linear combination of the oscillator functions to construct the eigenfunction. We can regard the criteria involved to be the following: to construct a low-lying eigenfunction we look for basis states with low energy and with a strong amplitude in the correct region, so that the potential can mould the eigenfunction out of the basis functions. For the present calculation these two requirements are to some extent in opposition, since n has to be sufficiently high before the basis states in the outer well have sufficient amplitude for the potential to be able to combine them correctly into the proper eigenfunction. The consequence of these competing requirements is that, for example, the ground state wavefunction is mainly formed from basis functions with n values in a 'window' between 40 and 60. Similar, but wider, windows occur for the first few excited states, but with an extra feature, namely that within the window several basis functions have very small amplitudes and their n values are symmetrically distributed within the window.

At present we have not found a conclusive theoretical explanation of this unexpected phenomenon, but we suspect the presence of a 'tuning' effect, in which a set of the basis functions have nodes near or at the centre of the outer wells and thus contribute weakly to the required linear combination. The simple technique for finding $\langle x^2 \rangle$ is particularly valuable here. It shows up with clarity which energy levels correspond to 'inner' and 'outer' wavefunctions. Moreover, it is possible to extend the technique even further, to compute individual components of the *normalized* eigencolumn. This is a feature which does not seem to have been pointed out before, although it is analogous to the method of Boolean functions which we have developed for finite-difference calculations [15].

If the element $H(J, K)$ of the H matrix is increased by a small amount α, the resulting change in the eigenvalue E will be given to first order by the expectation value of the perturbation using the correct normalized eigencolumn, with elements $A(J)$. This is readily seen to be the product $\alpha A(J) A(K)$ and thus leads to a product of eigencolumn elements. This direct energy shift method to find such products can be extended, as adding α to the diagonal element $H(J, J)$ will lead to the square of the normalized $A(J)$, while the total contribution from the states in a band is found by shifting equally all the diagonals for that band. The use of this technique confirmed the results concerning eigencolumns which we obtained by directly

finding and normalizing the eigencolumns using inverse iteration via the folding algorithm. This gives us additional confidence in the accuracy of our reported findings.

We note that although our calculation is evidently more complicated than the earlier double-well calculations [13, 14], it does share with them the simplifying feature that separating the even- and odd-parity calculations allows small energy-level splittings to be found from the results of separate calculations, rather than by direct calculation. We note further that only single or doubly degenerate levels appear in our calculated results. The even parity of V means that the inner well even and odd functions will only combine with the single appropriate + or − combination of the outer well functions, if we revert to the distributed basis picture, which of course we have avoided in our calculations. The different curvatures of the inner and outer wells render this mixing very small indeed, since they lead to 'local' oscillators with different level spacings. The result is that the lowest even–odd pairs belong to the outer wells and are degenerate to the accuracy quoted.

The interesting phenomena illustrated by these calculations and the way in which they lend themselves to an interpretation based on semi-physical reasoning indicate that the method of matrix construction applied here is a reliable technique for use with polynomial potentials. In particular, we believe that the very small splittings for the triple-well problem would be more difficult to compute and would require larger basis sets within the HEG formalism.

4. Concluding remarks

As reported above, our work contains several *internal* checks for consistency. Nevertheless, we have used two types of *external* check to confirm our numerical results. First, we have applied the finite-difference method of [16], which can handle even- and odd-parity states separately. The results confirm those given in our tables for both E and $\langle x^2 \rangle$ for both potentials. For the second test, we have applied the hypervirial perturbation approach [9, 17] to both potentials. The values of E and $\langle x^2 \rangle$ for the Gaussian potential (table 1) have been confirmed to all the quoted digits. For the second test potential, namely that of equation (10) with $U = 90$, some particularly interesting results emerged. On physical grounds we would expect the lowest levels to have wavefunctions which correspond closely to those for an isolated deep well. Accordingly, we have carried out a perturbation calculation using the centre of the right-hand deep well (at $x \approx 3.25$) as the origin and with the appropriate local quadratic potential as the unperturbed potential. The results give a dramatic confirmation of those in table 3. All the energy levels found correspond to 'outer' levels as indicated by the $\langle x^2 \rangle$ values in table 3. The lowest three levels agree exactly with those of table 3, to all the quoted digits. Although the next two energies are not given to so many converged digits by the perturbation calculation, they are obtained with sufficient accuracy to see that they are close to the average of the even- and odd-parity levels obtained by the matrix diagonalization calculation.

Although the results given for the triple-well problem used a basis set with $\beta^2 = 90$, we did use several other choices of β^2. The use of $\beta^2 < 90$ permits the calculation of the low-lying states with a basis of smaller dimension. Nevertheless, the lowest states still turn out to be composed of basis functions with a band of high n values. The choice $\beta^2 = 90$ illustrates most clearly the phenomenon of 'artificial convergence'. The usual empirical test in matrix calculations is to assume that convergence has been achieved when the lowest few levels become stable to a high number of decimal digits. This stability is achieved in the triple-well calculations, yet the physical shape of the potential function suggests that there ought to be some states below the apparently stable 'ground state'. Increasing the number of basis states further does not affect the stability of the supposed ground state but leads to the gradual emergence and stabilization of lower states which are associated with wavefunctions trapped

in the deep outer wells. It then emerges that the original 'ground state' is, in fact, the seventh true eigenvalue! If the x coordinate is scaled by a factor k, then the potential $90x^2 - 20x^4 + x^6$ becomes $90k^4x^2 - 20k^6x^4 + k^8x^6$, while the energy is multiplied by a factor k^2. Since there is a one-to-one mapping between the scaled and unscaled problems, the number of basis functions needed to obtain convergence of the nth eigenvalue would not be affected if we took the basis to have $\beta^2 = 90k^4$ to make it match perfectly to the physical shape of the inner well potential.

Two points emerging from the Gaussian potential calculations clearly merit further investigation. First, the interpretation of the results for odd M values and the extent to which they give useful lower bounds, in general, remains to be studied in more detail. Secondly, although the results of table 2 take the M values right up to explicit convergence, the smooth behaviour of the data strongly suggests that the limiting energy might be obtainable with less effort by applying a Wynn algorithm [9] or some other summation approach to a sequence of results for lower M values. This would then make it possible to obtain results for some higher states which would require very high M values to obtain explicit convergence.

Acknowledgment

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