A perturbation approach to finite difference methods

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Abstract   A perturbation theoretic approach to finite difference methods for the calculation of eigenvalues is shown to permit an increase in the accuracy of the calculations and also to make possible the calculation of expectation values along with the eigenvalues. An application of the virial theorem can then boost the order of accuracy of any given finite difference method. Integrated probabilities and point values of the normalized wavefunction can be found without any use of quadratures. Illustrative examples are given involving the Schrodinger equation for simple polynomial potentials.

Keywords   Finite differences · Quantum mechanics · Energy levels

1 Introduction

In recent review articles Simos and coworkers [1,2] have described accurate high order finite difference methods for the calculation of the eigenvalues of the Schrodinger equation. These review articles give details of the many preceding works in which Simos has developed his techniques for high order methods.

The present work mainly deals with an ancillary problem, that of the calculation of expectation values. Although the techniques developed are studied within the context of low order finite difference methods they are also applicable (in their external

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differentiation form) to the high order methods developed by Simos. The traditional method of boosting the effective order of a second or fourth order finite difference method is to apply Richardson extrapolation to the results of a sequence of calculations which use gradually decreasing steplengths h. The principal aim of the present work is to see how far the use of perturbation theory can help in improving and extending the basic low order finite difference methods used within this Richardson extrapolation framework.

Section 2 shows how the oldest traditional second order method for eigenvalue calculation (often called Hartree's method) can be extended to fourth order while still retaining the simple three term recurrence relation form of the original Hartree method. Section 3 then looks at the calculation of expectation values, explaining how "external" and "internal" approaches are possible. Section 4 gives some further computational details Sect. 5 shows how the use of the virial theorem in conjunction with calculated expectation values allows the order of a given finite difference method to be increased by two.

Section 6 deals with the interesting case of formally singular perturbations; it is found possible to calculate both integrated probabilities for selected regions of space and also to calculate the square of the normalised wavefunction at a selected point. The novelty of the method is that no integrations are performed and no wavefunction values are stored during the calculations! Sect. 7 gives a brief discussion.

2 From second order to fourth order

To simplify the later discussion we shall write the usual Schrodinger equation

$$-\alpha D^2 \Psi + V\Psi = E\Psi \tag{1}$$

in the form

$$\Psi^{(2)} = \alpha^{-1}(V - E)\Psi = P\Psi \tag{2}$$

and shall study the large class of finite difference methods which use a step length h which does not vary with position. We start from the equation

$$\Psi(x + h) + \Psi(x - h) - 2\Psi(x) = h^2\Psi^{(2)} + (1/12)h^4\Psi^{(4)} + \cdots \tag{3}$$

The traditional second order method uses only the first term in the Taylor series on the right and leads to the recurrence relation

$$\Psi(x + h) = [2 + h^2 P(x)]\Psi(x) - \Psi(x - h) \tag{4}$$

Inspecting the h^4 term in the Taylor series we find (on using (2))

$$\Psi^{(4)} = (P\Psi)^{(2)} = P^2\Psi + [P^{(2)} + 2P^{(1)}D]\Psi \tag{5}$$

The terms in the square bracket give the contribution due to the local derivatives of the potential. First order perturbation theory gives the energy shift caused by these terms regarded as a perturbation. Integrating by parts the product $2\Psi P^{(1)}\Psi^{(1)}$ over the region of the x axis being used shows that it exactly cancels the integral of the product $\Psi^2 P^{(2)}$, provided that at the end points either Ψ is zero (Dirichlet conditions) or $P^{(1)}$ is zero (a potential maximum or minimum). Thus the first order contribution to the energy eigenvalue from the terms in the square bracket is zero; they contribute in second order of perturbation (which means at order h^8). We can thus obtain a simple fourth order method by just adding in the first term arising in (5), giving

$$\Psi(x + h) = [2 + F + (1/12)\text{ß}F^2]\Psi(x) - \Psi(x - h) \tag{6}$$

where $F = h^2 P$ and where the parameter ß (0 or 1) can turn on or off the fourth order accuracy. This allows us to test our perturbation theoretic prediction. A shooting calculation over the range $x = -10$ to $x = 10$ for the simple potential $V = x^2$ and with α equal to 1 using the numbers of strips NS $= 128$ and 256 gave the following energies

(NS = 128)	(ß = 0)	0.9984717821	(ß = 1)	0.9999949899
(NS = 256)	(ß = 0)	0.9996183846	(ß = 1)	0.9999996866

Since we know that the exact ground state energy should be 1 we can work out the error in each of the above results. The error ratio for the ß $= 0$ pair of results is 4.00, while that for the ß $= 1$ results is 15.99, illustrating the respective second and fourth order accuracy of the two calculations. Doing an appropriate extrapolation based on these powers 2 and 4 gives an energy estimate 1.0000005854 from the two second order results and an energy estimate 0.9999999997 from the two fourth order results.

We should note here that the well-known Numerov approach, which makes a finite difference expansion of $\Psi^{(4)}$ as the second derivative of $\Psi^{(2)}$, is expressible in the style of Eq. 6 by putting $(2 + (5/6)F)/(1 - (1/12)F)$ in the square bracket. The method derived above by perturbation theory agrees with this function up to the h^4 term and our theory correctly predicts that the disagreement in later terms does not change the basic h^4 accuracy of the method. The terms in the square bracket in (6) are the initial terms in the series for $(1/2)\cos(F)$ (for $F > 0$) or $(1/2)\cosh(F)$ (for $F < 0$); one can also use these functions in what might be called a full constant potential approximation. However, the basic h^4 accuracy persists through all these elaborations.

3 Expectation values. internal and external methods

In the preceding discussion we have used the conventional Greek symbol Ψ for the wavefunction. This symbol is not part of the usual lexicon of symbols used in writing computer programs. Since we shall begin to describe some of the computational details used in calculations we now change to the symbol W (for wavefunction).

For the discussion of this section we add into the potential a "dummy" perturbing term μU, so that the function F appearing in (6) becomes

$$F = \alpha^{-1} h^2 (V + \mu U - E) = h^2 P \tag{7}$$

In our changed notation Eq. 6 becomes

$$W(x + h) = [2 + F + (1/12) \text{ß} F^2] W(x) - W(x - h) \tag{8}$$

We now differentiate the above equation throughout with respect to E, denoting the derivative of W with respect to E by WE. Besides the simple terms involving WE we also have a contribution form the square bracket in (8), which we can evaluate by looking at (7). A simple use of the chain rule can be used to evaluate that term. If for brevity we denote the terms in the square bracket by [ ] then we conclude that WE obeys the recurrence relation

$$WE(x + h) = [\ ] WE(x) - WE(x - h) - h^2 \alpha^{-1} (1 + (1/6) \text{ß} F) W(x) \tag{9}$$

Similarly differentiating with respect to μ and denoting the derivative of W with respect to μ by WU we find that the WU values obey the recurrence relation

$$WU(x + h) = [\ ] WU(x) - WU(x - h) + h^2 \alpha^{-1} (1 + (1/6) \text{ß} F) U(x) W(x) \tag{10}$$

To initiate the three recurrence relations at some starting point x = X at which we set W(X) = 0, W(X + h) = 1 (or h if preferred) we simply set the values of WE and WU equal to zero at both X and X + h. At the other end of the range (x = L) we want to adjust the trial E so as to make W(L) zero. We correct the initial trial E by the following assignment statement form of Newton's rootfinding method:

$$E := E - W(L)/WE(L) \tag{11}$$

If we recall that from simple first order perturbation theory a slight change $d\mu U(x)$ will give the energy change $d\mu < U >$ (where $< U >$ is the expectation value of U(x)) then we can see that we find $< U >$ by working out the partial derivative of E with respect to μ. A little manipulation of partial derivatives leads to the equation

$$< U > = -WU(L)/WE(L) \tag{12}$$

Equations 10 and 12 are often used for a function U(x) which does not even appear in the Schrodinger equation, which is why the term μU in (7) was described as a dummy term.

The method described above we call the internal method. It is entirely energy based and thus does not involve the quadratures which are commonly used to work out expectation values. The three recurrence relations can be propagated together and require only one common evaluation of the F terms per step. Care must be taken to work out the new WE and WU values before the new W value, since the new WE and WU are

coupled to the preceding W (not to the new one). The perturbative ideas used above make it clear that an external approach is possible. If a method of calculation of the energy eigenvalues is so complicated that the above internal differentiation process would be difficult (as can occur for very high order finite difference methods or for matrix eigenvalue methods) then the direct addition of a small term of the form μU to the Hamiltonian treated will give a first order energy shift of $\mu <U>$.

If the calculational method is of high accuracy (such as the high order methods developed by Simos) then a sufficiently small μ value can be used to give accurate expectation values. In a finite difference approach the U term can be incorporated directly whereas in a matrix approach the matrix elements of U will need to be known. This external approach has indeed been used in some matrix eigenvalue works [3,4].

4 Scaling and recycling

It is important to note three principal features of the energy based approach which has been described in this work by making repeated applications of perturbation theory. First, it permits the calculation of expectation values without any quadratures and without even the need to store any wavefunction values. Second, since the Eqs. 11 and 12 involve only ratios of quantities, it is permissible to scale the values of W,WE and WU simultaneously at any point so as to avoid overflow or underflow : this scaling has no effect on the final results calculated at x = L. (We note that a scaled Numerov method due to Johnson already exists [5]). Third, since the method is based on a three term recurrence it is possible to economize on storage by using the numerical labels 1,2,3 for the three values appearing in (8), (9) and (10). At each step the same labelling can be recycled by setting $W(J) = KW(J+1)$ for J = 1 to 2, before calculating the new W(3). Here K is the scaling factor and the same cycling is carried out for the WE and the WU. The consequence of these simplifications is that only a very small computer memory capacity is needed (indeed a pocket computer can be used). The scaling process makes it possible to use forward shooting to find energy levels even for potentials which have a sequence of broad barriers between deep wells, as was demonstrated for the difficult potential $\cos(x^{1/2})$ [6].

As a simple example of the methods of the preceding sections we give a few results obtained by treating the potential $V = x^4$ in the region x = −5 to x = 5. We take $\alpha = 1$ and use the ß = 1 (fourth order) method, together with a number of steps NS equal to 64,128 and 256.

$$(NS = 64) \quad E = 1.0603353393 \qquad <x^2> = 0.3620185090$$
$$(NS = 128) \quad E = 1.0603604007 \qquad <x^2> = 0.3620223888$$
$$(NS = 256) \quad E = 1.0603619846 \qquad <x^2> = 0.3620226325$$

We find that the difference ratios of both the E values and the $<x^2>$ values are almost exactly 16 (indicating the h^4 error). Richardson extrapolation of the results gives the accurate values E = 1.0603620905 and $<x^2> = 0.3620226483$.

5 Using the virial theorem

The virial theorem for an enclosed system (with $-R < x < R$) is

$$2E = <2V + xV^{(1)}> -R(dE/dR) \qquad (13)$$

Since we can find both E and the expectation value on the right we can find dE/dR if required for the study of an enclosed system. For "infinite" space and bound states we can drop the dE/dR term and thus arrive at the conclusion that the energy equals an expectation value. For example, if we take the potential $V = x^2$ with $\alpha = 1$ then we find that E should equal $2 <x^2>$ or for $V = x^4$ we should have $E = 3 <x^4>$. Since we know the exact groundstate energy for the x^2 case to be 1 we shall treat that case first.

Using the range $x = -10$ to $x = 10$ we find for NS $= 256$ the following results:

$$(\text{ß} = 0) \quad E = 0.99961838459 \quad 2 <x^2> = 0.99923662332$$
$$(\text{ß} = 1) \quad E = 0.99999997979 \quad 2 <x^2> = 0.99999993937$$

The errors of the two different energy estimates are seen to be in the almost exact ratios 2 to 1 for ß $= 0$ and 3 to 1 for ß $= 1$ and this numerical observation has been explained by a theoretical treatment [7], valid for any smooth V. To boost the ß $= 0$ method to a fourth order one (a new and different one!) we could form the linear combination of terms $2E - <V + x\ V^{(1)}/2>$ during the calculation, since we can calculate the expectation value along with the energy. To boost the ß $= 1$ method to a sixth order one we form the linear combination $(3E - <V + xV^{(1)}/2>)/2$. Applying this formula to the results shown above for ß $= 1$ gives exactly 1 for the energy.

Using NS $= 512$ for the potential $V = x^4$ from $x = -5$ to $x = 5$ gives the results

$$(\text{ß} = 1) \quad E = 1.06036208386 \quad 3 <x^4> = 1.06036207062$$

Forming the linear combination $(3E - 3 <x^4>)/2$ then produces from the above data the improved result E $= 1.06036209048$, correct to all digits.

For a polynomial potential it is only necessary to make an explicit calculation of one or two $<x^N>$ for low N, since the higher $<x^N>$ can be found by using the hypervirial relations:

$$(1/2)\alpha N(N^2 - 1) <x^{N-2}> +(2N + 2)E <x^N>$$
$$= \sum (2N + 2 + M)V(M) <x^{N+M}> \qquad (14)$$

for the case of a potential which is a sum of terms $V(M)x^M$.

6 The incremental form. singular perturbations

Inspection of the Eqs. 8–10 from a computational point of view suggests that the leading term 2 in the square bracket might dominate the other terms, which have powers of

h as factors. This problem can be avoided by using an incremental form of (8) involving paired equations and the quantity $DW(x) = W(x + h) - W(x)$:

$$DW(x) = [F + (1/12)ßF^2]W(x) + DW(x - h) \qquad (15)$$
$$W(x+h) = W(x)+DW(x) \qquad (16)$$

with similar incremental equations for the WE and WU (and, of course, if desired, with the scaling and recycling adjustments given in Sect. 4). The incremental form of the equations is more accurate than the direct form if a fixed number of digits of precision is being used (as in standard double precision).

By considering the effect of a delta function in producing a point discontinuity of the gradient of the wavefunction or by thinking of it as a very thin rectangle of unit area at a point we reached the conclusion that the singular perturbation due to a delta function at an arbitrary point $x = X$ can be simulated in our approach by using as the U function a function which equals 1/h at $x = X$ and is zero everywhere; it thus varies with the step length h being used. The expectation value of a delta function at $x = X$ can easily be seen to be the square of the normalized wavefunction at $x = X$. This form of U does in fact turn out to be correct and leads to an amusing and surprising consequence. We have constructed a method which stores no wavefunctions and performs no quadratures to find expectation values or normalized wavefunctions. Nevertheless we can find the squared normalized wavefunction at a grid point by what is in essence a purely energy based technique based on first order perturbation theory. For the groundstate of the potential $V = x^2$ we know that the wavefunction is a constant times $\exp(-x^2/2)$. Integration quickly gives the normalization constant and so shows that the squared wavefunction at the origin is $\pi^{-1/2}$. Using the region $x = -10$ to $x = 10$ and the appropriate U function (equal to 1/h at $x = 0$) we find the value of the squared wavefunction at the origin to be 0.564189583548, which agrees with the analytical value to all digits. For the potential x^4 we expect a more compact wavefunction; we find the square of the wavefunction at the origin to be 0.628751369373.

After the delta function the obvious next candidate for study is the Heaviside function. The expectation value of the Heaviside function $H(x - X)$ is clearly equal to the integral of the square of the wavefunction between X and the upper limit of the region used. It is thus the quantum mechanical integrated probability for that region.

The appropriate U function to simulate $H(x - X)$ involves a linear ramp at X:

$$U(X - Nh) = 0; \quad U(X) = 0; \quad U(X + Nh) = 1 \quad (N \geqslant 1)$$

This integrated probability for $x > 0$ is of interest when an odd perturbation such as λx or λx^3 is applied to an initially symmetric potential (the cases of double well systems eg models of the hydrogen bond or the ammonia molecule [8] are of particular interest). Here we give just one simple example related to our previous ones. If we set $V = x^4 + \lambda x$ with $\alpha = 1$ and use the region $x = -5$ to $x = 5$ then our Heaviside form of U gives for the integrated probability for $x > 0$ (initially 0.5 at $\lambda = 0$) the values 0.4998192257 at $\lambda = 0.001$ and 0.4996384515 at $\lambda = 0.002$, showing a linear variation at small λ. Changing over to $\lambda = -0.001$ and -0.002 gives the correct complementary values of 0.5001807743 and 0.5003615485 respectively.

7 Conclusion

The present review brings together in a more coherent form several ideas which have been developed in a somewhat piecemeal manner in some previous works [9–11].

The unifying theme which turned out to be the most useful was that of the application of first order perturbation theory to finite difference methods for energy eigenvalues;

We have shown how many numerical results can be obtained without using the traditional approach of quadratures involving a stored wavefunction.

We have used Dirichlet boundary conditions throughout to give a clear explanation of the energy-based approach. For a symmetric potential it is easy to isolate the even parity states by using the negative half axis and rendering zero the difference quantity W(−h)−W(h) at the two points closest to the origin. This enables the calculation of small even—odd splittings for symmetric double well systems.

We should note that in our exposition we have used the shooting approach to finite difference relations, rather than the matrix eigenvalue formulation of them. In other work [12] we have shown how the interplay between the shooting and matrix approaches can give useful insights into high order finite difference methods.

References

1. Z.A. Anastasi, D.S. Vlachos, T.E. Simos, J. Math. Chem. **46**, 621 (2009)
2. Z.A. Anastasi, D.S. Vlachos, T.E. Simos, J. Math. Chem. **46**, 652 (2009)
3. R.K. Pathak, A.K. Chandra, K. Battacharyya, Phys. Rev. A **48**, 4097 (1993)
4. R. Chen, H. Guo, Chem. Phys. Lett. **308**, 123 (1999)
5. B.R. Johnson, J. Chem. Phys. **67**, 4086 (1977)
6. J.P. Killingbeck, N.A. Gordon, M.R.M. Witwit, Phys. Lett. A **206**, 279 (1995)
7. J.P. Killingbeck, G. Jolicard, Phys. Lett. A **228**, 205 (1997)
8. A. Lakhlifi, Eur. Phys. J. D **8**, 211 (2000)
9. J. Killingbeck, J. Phys. B At. Mol. Phys. **15**, 829 (1982)
10. J. Killingbeck, J. Phys. A Math. Gen. **20**, 1411 (1987)
11. J. Killingbeck, J. Phys. A Math. Gen. **21**, 3399 (1988)
12. J.P. Killingbeck, G. Jolicard, J. Phys. A Math. Gen. **41**, 125204 (2008)