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COMMENT

Boolean functions and finite difference eigenvalues

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Abstract. Finite difference calculations involving the expectation values of Boolean functions are shown to yield detailed information about the properties of the energy levels and eigenfunctions for double-well potentials.

1. Introduction

In a recent letter Diaz *et al* (1988) described a finite difference method of numerical integration for the Schrödinger equation

$$-\alpha D^2\psi + V\psi = E\psi \quad (1)$$

which involves the computation of two linearly independent solutions $A(x)$ and $B(x)$. They state that the new method is required because the more simple finite difference method of Killingbeck (1985a) is not applicable to potentials $V(x)$ of mixed parity. We wish to point out in this work that the simple method is *not* thus limited; it works just as easily for the potentials treated by Diaz *et al* (1988) as it does for potentials of even parity. The introduction of a different (two-variable) method for mixed parity potentials is thus unnecessary.

The test potentials used by Diaz *et al* (1988) came from the work of Somorjai and Hornig (1962), who used double-minimum model potentials to describe proton motion in hydrogen bonds. Somorjai and Hornig (1962) discussed various resonance phenomena caused by coupling between the left- and right-well states in a double-well potential. They calculated the energy levels by using a 20×20 secular matrix in a basis of harmonic oscillator functions centred on $x = 0$. Comparison of the works of Diaz *et al* (1988) and Somorjai and Hornig (1962) shows that the former authors used units for which $\alpha = 2$ in equation (1), although this unconventional choice was not clear from their discussion. For purposes of comparison we use the same choice in our numerical tables, which illustrate how the use of Boolean functions in a finite difference approach can reveal information which is not easily obtainable by the matrix diagonalisation approach of Somorjai and Hornig (1962). The methods which we describe are readily applicable on modern microcomputers, which can handle both Boolean and mathematical functions. Our convention in the present work is

$$\text{True} \equiv 1; \text{False} \equiv 0 \quad (2)$$

and readers will easily make the appropriate modifications for computers which use a value of -1 to represent True.

Section 2 describes briefly the calculational algorithm, which involves only a slight modification of that described by Killingbeck (1985b). Section 3 explains the novel use of Boolean functions to calculate some relevant quantities. Section 4 gives some illustrative numerical results which indicate the value of the technique for exploring various subtle aspects of the theory of double-well potentials, and also reports the result of an interesting calculation using perturbation theory.

2. The finite difference calculation

The way in which a finite difference calculation can yield an eigenvalue of a potential $V(x)$ together with the expectation value of any selected function $U(x)$ has been explained in detail by Killingbeck (1985b), and so we recapitulate here only the main details of the method. Taking the most simple finite difference representation of $D^2\psi$ in the Schrödinger equation (1) yields the familiar three-point recurrence relation

$$\psi(x-h) = F(x)\psi(x) - \psi(x+h) \quad (3)$$

where

$$F(x) = 2 + \phi + \frac{1}{12}K\phi^2 \quad (4)$$

$$\phi(x) = \alpha^{-1}h^2(V(x) - E) \quad (5)$$

h being the finite difference step length. The choice $K = 0$ in (4) gives the traditional (h^2 error) method, while the choice $K = 1$ gives the more accurate (h^4 error) method of Killingbeck (1985b).

The method of Killingbeck (1985b) hinges on the differentiation of equation (3) with respect to E and also with respect to λ , with the potential $V(x)$ in (1) being regarded as having a dummy term $\lambda U(x)$ added to it. Denoting the appropriate derivatives of ψ by ψ_E and ψ_λ , we obtain the recurrence relations

$$\psi_E(x-h) = F(x)\psi_E(x) - \psi_E(x+h) - G(x)\psi(x) \quad (6)$$

$$\psi_\lambda(x-h) = F(x)\psi_\lambda(x) - \psi_\lambda(x+h) + G(x)U(x)\psi(x) \quad (7)$$

where

$$G(x) = \alpha^{-1}h^2(1 + \frac{1}{6}K\phi(x)). \quad (8)$$

To use equations (3), (6) and (7) to solve equation (1) with the boundary conditions $\psi(x_2) = \psi(x_1) = 0$ (with $x_1 < x_2$) we set $\psi(x_2) = 0$, $\psi(x_2-h) = h$, with all ψ_E and ψ_λ zero, and use the recurrence relations to calculate the three ψ functions for decreasing x down to x_1 . Some trial E value has to be used to start the calculation, but at the end of the run it is revised by the Newton method formula

$$E' = E - \psi(x_1)/\psi_E(x_1) \quad (9)$$

while the expectation value of U is given by the formula

$$\langle U \rangle = -\psi_\lambda(x_1)/\psi_E(x_1). \quad (10)$$

If the Neumann (zero-gradient) boundary condition is to be obeyed at x_1 then the quantity $\psi(x_1+h) - \psi(x_1-h)$ (and its corresponding partners) replaces $\psi(x_1)$ in (9) and (10). To treat an even parity potential with $x_2 = L$, $x_1 = 0$ we can use a Neumann condition at $x_1 = 0$ to pick out the even parity states. We *could* also use a Dirichlet condition with $x_1 = -L$, and then the method still works even if the potential is not

symmetric about $x = 0$. The only requirement is that the bound state amplitude shall be negligible outside the region $L > x > -L$, in which case we find that both Dirichlet and Neumann boundary conditions at x_1 give the same results. An asymmetric potential is thus handled by adjusting x_1 and does not need the separate technique described by Diaz *et al* (1988).

3. The use of Boolean functions

For double-well problems of the type studied by Somorjai and Hornig (1962) it would be useful to have values for numerical quantities such as $\psi^2(0)$ and the 'left-hand probability'

$$P = \int_{-\infty}^0 \psi^2(x) dx. \tag{11}$$

We have carried out theoretical analysis and computer experiments to find the appropriate functions $U(x)$ to use in the formalism of § 3. The appropriate functions simulate a Dirac delta function and a Heaviside function, respectively, and can be described as follows. $\psi^2(0)$ is the expectation value of the function

$$U(x) = \begin{cases} h^{-1} & \text{at } x = 0 \\ 0 & \text{for } x \neq 0 \end{cases} \tag{12}$$

while P is the expectation value of the function

$$U(x) = \begin{cases} 1 & x \leq -h \\ \frac{1}{2} & x = 0 \\ 0 & x > 0. \end{cases} \tag{13}$$

If the interval $-L < x < L$ contains N strips of length h , with a running index M which goes from $N - 1$ to 0 to traverse the interval (so that $x = x_1 + Mh$) then the functions of equations (12) and (13) take the simple Boolean forms (with $N2 = N/2$)

$$(M = N2)/h \tag{14}$$

and

$$(M \leq N2 - 1) + (M = N2)/2. \tag{15}$$

Computational tests using these functions with the $K = 1$ method of § 3 revealed that the values of E and $\psi^2(0)$ both have errors of h^4 type for small h , while the value of P has an error of h^2 type. Given these facts it is easy to obtain highly accurate results for all the cases treated by Diaz *et al* (1988) by using $N = 50$ and $N = 100$ with one stage of Richardson extrapolation (Killingbeck 1985a). For the test potential $V(x) = x^2$, with $L = 5$ and $N = 50$ and 100, we obtained $\psi^2(0) = 0.564\ 1896$, which agrees with the analytical result to the accuracy quoted.

4. Some double-well calculations

We take as our test case the Schrödinger equation

$$-2D^2\psi + (2x^4 + \mu x^3 - 14x^2)\psi = E\psi \tag{16}$$

which was studied at $\mu = 1$ by both Diaz *et al* (1988) and Somorjai and Hornig (1962). We found that varying μ gives rise to some interesting effects. Table 1 shows our

Table 1. Results for the two lowest energy levels of the Schrödinger equation (16), with $x_1 = -5$, $x_2 = 5$, using 50 and 100 strips in the finite difference method.

	$\mu = 0$	$\mu = 0.001$	$\mu = 0.002$
E	-17.342 211	-17.344 155	-17.348 546
P	0.500 001	0.788 548	0.908 103
$\psi^2(0)$	0.001 503	0.001 364	0.001 183
E	-17.324 905	-17.322 963	-17.318 578
P	0.500 000	0.211 453	0.091 899
$\psi^2(0)$	0	0.000 130	0.000 320
E_L	-17.324 905	-17.331 038	-17.337 174
E_R	-17.324 905	-17.318 773	-17.312 643

calculated results for μ values near zero, while table 2 shows our results for some larger μ values. The quantities E_L and E_R are energy levels computed with the (x_1, x_2) pairs $(-5, 0)$ and $(0, 5)$ respectively, so that the actual energies for $(x_1, x_2) = (-5, 5)$ indicate the effect of removing a barrier at $x=0$ to allow tunnelling to take place between left and right wells.

In a simple 2×2 matrix approach to the calculation of the energy levels for small μ (table 1) we could take the even parity and odd parity states at $\mu = 0$ as basis states, with μx^3 as the off-diagonal perturbation. A simple calculation shows that such a model would predict an energy splitting

$$\Delta = [(0.017\ 306)^2 + 4\mu^2 M^2]^{1/2} \quad (17)$$

where M is the matrix element of x^3 between the basis functions. Our finite difference results for small μ fit very accurately to the formula (17) with $M = 6.116$. The values of P and $\mu^2(0)$ in table 1 show how the ground state, which arises from the even parity state, becomes localised in the deeper left well as μ increases from zero.

Table 2 shows the lowest three levels, since in the vicinity of $\mu = 1.13$ the lowest level in the right well shows a resonance effect with the second level in the left well.

Table 2. Results for the first three energy levels in the neighbourhood of $\mu = 1.13$, with the same parameters as for table 1.

	$\mu = 1.00$	$\mu = 1.10$	$\mu = 1.15$
E	-24.517 598	-25.367 009	-25.801 690
P	0.999 989	0.999 992	0.999 993
$\psi^2(0)$	0.000 073	0.000 056	0.000 049
E	-12.091 375	-11.660 074	-11.684 748
P	0.002 571	0.027 179	0.947 101
$\psi^2(0)$	0.004 957	0.007 270	0.009 400
E	-10.573 721	-11.289 801	-11.422 870
P	0.996 026	0.972 230	0.052 670
$\psi^2(0)$	0.009 186	0.005 551	0.002 965
E_L	-24.516 590	-25.366 222	-25.800 997
E_L	-10.488 993	-11.228 643	-11.607 578
E_R	-12.046 121	-11.601 218	-11.383 699

The P values indicate how the second energy level jumps from right to left as μ rises through the resonance region.

The renormalised hypervirial perturbation method (Killingbeck 1987) can easily be modified to deal with the case of a harmonic oscillator perturbed by a sum of x^3 and x^4 type potentials. We have applied it to the ($\mu = 0$) potential $-14x^2 + 2x^4$ which, when expanded about the right-hand minimum, takes the form

$$V = -\frac{49}{2} + 28x^2 + 8\left(\frac{7}{2}\right)^{1/2}x^3 + 2x^4. \quad (18)$$

Treating the last two terms as the perturbation, we can ask: to which energy level will the perturbation series fit? The function V in (18) *fully* describes the potential, including the left-hand well, but our unperturbed state based on the right-hand well does not have the correct symmetry appropriate to the full perturbed potential. In fact our perturbation calculation gave $E = -17.3336$, which is exactly the average of the even and odd parity energies. We conjecture that this result may have some relevance for those approaches which treat the H_2^+ ion in terms of a hydrogen atom being perturbed by the electrical field of a proton.

The specimen calculations reported here show that local quantities such as $\psi^2(0)$ (or ψ^2 at any selected x value) and integrated quantities such as P can be computed without the explicit tabulation of ψ or the estimation of normalisation integrals. The techniques used can be applied to other asymmetric potentials such as the asymmetric oscillator potential discussed by Crosignani and Di Porto (1988).

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