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**LETTER TO THE EDITOR**

# On the numerical integration of the Schrödinger equation

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**Abstract.** A finite-difference method for solving the Schrödinger eigenvalue equation is generalised in order to treat a larger number of potentials. Results are shown for asymmetrical two-well oscillators.

There are at present several powerful methods for solving one-dimensional eigenvalue problems. Among them, those that can be run on small microcomputers have recently received much attention (see [1, 2] and references therein). In particular, Killingbeck's method [1, 2] has recently proved to be suitable for treating difficult two-point boundary value problems [3].

In its present form, Killingbeck's method is rather limited because it does not apply to one-dimensional quantum mechanical models with potentials that are not parity invariant. The purpose of this letter is to develop a generalised version of this procedure that is free from this drawback.

We consider the eigenvalue equation

$$F''(x) = Q(E, x)F(x) \tag{1}$$

where $Q(E, x) = V(x) - E$, with the boundary conditions

$$F(a) = F(b) = 0 \qquad a < b. \tag{2}$$

Following Killingbeck [1, 2] we calculate $F(x+h)$ in terms of $F(x)$ and $F(x-h)$ from

$$F(x+h) = G(E, h, x)F(x) - F(x-h). \tag{3}$$

If $G$ is chosen to be (the discussion below also holds for larger-order perturbation approaches [2])

$$G(E, h, x) = 2 + h^2 Q(E, x) + \tfrac{1}{12}h^4 Q(E, x)^2 \tag{4}$$

then the eigenvalue error is $O(h^4)$ as $h \to 0$ [1] provided that the starting point is sufficiently accurate.

When $b = -a$ and $V(-x) = V(x)$ the appropriate starting point is obtained from the relation $F(-h) = \pm F(h)$ [1, 2]. In order to treat other cases we propose to make use of the fact that $F(x)$ can be written

$$F(x) = A(x) + cB(x) \tag{5}$$

  

where $A$ and $B$ are two linearly independent solutions of (1) satisfying

$$A(x_0) = B'(x_0) = 1 \qquad A'(x_0) = B(x_0) = 0 \tag{6}$$

for an arbitrary $x_0$ value belonging to $(a, b)$. After introducing (5) into (2) we have

$$A(a)B(b) - A(b)B(a) = 0. \tag{7}$$

The starting point for the finite difference process is easily obtained from

$$F'(x) = \{[F(x+h) - F(x-h)]/(2h)\} - (h^2 F'''(x)/6) + O(h^4)$$
$$F'''(x) = Q'(E, x)F(x) + Q(E, x)F'(x)$$

and equation (3). For instance, a straightforward calculation shows that

$$A(x_0 - h) = \tfrac{1}{2}G(E, h, x_0) - \tfrac{1}{6}h^3 Q'(E, x_0) + O(h^4)$$
$$B(x_0 - h) = -h - \tfrac{1}{6}h^3 Q(E, x_0) + O(h^4). \tag{8}$$

The procedure is very simple. Beginning from (6) and (8) we proceed backwards and forwards with (3) for $A(x)$ and $B(x)$ in order to calculate $A(a)$,$B(a)$, $A(b)$ and $B(b)$. The roots $E(h)$ of (7) are close approximations to the actual eigenvalues if $h$ is small enough. The limits $E(0)$ are estimated by means of the Richardson extrapolation [4].

As an example we consider the potential

$$V(x) = 2(v_2 x^2 + v_3 x^3 + v_4 x^4) \tag{9}$$

which has two minima if $9v_3^2 > 32v_2v_4$. The boundary conditions $F(\pm\infty) = 0$ are replaced by $F(a) = F(b) = 0$, where $a \ll x_0 \ll b$, and $x_0$ is chosen to be the coordinate of the deepest minimum.

Some of the parameters $v_j$ considered by Somorjai and Hornig [5] are shown in table 1. Results for the lowest lying eigenvalues are compared in table 2. The interval

**Table 1.** Parameters $v_j$ for a number of asymmetrical two-well potentials $V_k$.

| | $V_6$ | $V_7$ | $V_8$ | $V_9$ | $V_{10}$ |
|---|---|---|---|---|---|
| $v_2$ | −5.1199 | −7.6284 | −7.0 | −7.77 | −7.905 |
| $v_3$ | 0.0152 | 0.3 | 0.5 | 0.4939 | 0.5812 |
| $v_4$ | 0.65 | 1.0 | 1.0 | 0.98 | 1.0 |

**Table 2.** Lowest eigenvalues $E_n$ for the potentials $V_k$ in table 1.

| | $n$ | Present | [5] |
|---|---|---|---|
| $V_6$ | 0 | −14.270 233 28 | −14.85 |
| | 1 | −13.827 382 03 | −14.40 |
| $V_7$ | 0 | −26.188 057 61 | −26.18 |
| | 1 | −17.711 668 82 | −17.71 |
| $V_8$ | 0 | −24.517 597 66 | −24.51 |
| | 1 | −12.091 375 08 | −12.09 |
| $V_9$ | 0 | −31.770 545 22 | −31.76 |
| | 1 | −16.808 918 63 | −16.80 |
| | 2 | −16.755 309 97 | −16.78 |
| $V_{10}$ | 0 | −33.862 386 35 | −33.85 |
| | 1 | −18.532 416 03 | −18.43 |

$b = -a = 4$ is found to be large enough for all the cases; and roots of (7) have been obtained through the bisection method (p 220 of [4]). The Richardson extrapolation [4] has been used to estimate $E(0)$ from $E(h)$, where $h = 0.05$, 0.02 and 0.01.

The algorithm here developed allows Killingbeck's method [1,2] to be applied to a wider class of quantum mechnical problems while retaining the simplicity that makes it suitable for microcomputer use.

## References

[1] Killingbeck J P 1979 *Comput. Phys. Commun.* **18** 211; 1982 *J. Phys. B: At. Mol. Phys.* **15** 829; 1983 *Microcomputer Quantum Mechanics* 2nd edn (Bristol: Adam Hilger) ch 10; 1985 *Rep. Prog. Phys.* **48** 54

[2] Killingbeck J P 1986 *Phys. Lett.* **115A** 301

[3] Killingbeck J P 1987 *J. Phys. A: Math. Gen.* **20** 1411

[4] Dahlquist G and Björck Å 1974 *Numerical Methods* (New York: Prentice-Hall) p 269

[5] Somorjai R L and Hornig D F 1962 *J. Chem. Phys.* **36** 1980