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1989 J. Phys. A: Math. Gen. 22 287

(http://iopscience.iop.org/0305-4470/22/3/012)

J. Phys. A: Math. Gen. **22** (1989) 287-295. Printed in the UK

On computing eigenvalues of the Schrödinger equation for symmetrical potentials

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Received 14 June 1988

Abstract. The problem of the numerical determination of eigenvalues of the one-dimensional Schrödinger equation with symmetrical potential $V(x)$ is considered. The problem is reduced to the definition of an 'eigenvalue function' $G(E)$ well defined for the given potential V. It is theoretically proved that the even-parity eigenvalues are given by $G(E)=0$, and the odd-parity eigenvalues are given by $G(E)=\infty$. The method is 'canonical' in the sense that it is independent of the eigenfunction; yet, along with the eigenvalue, it allows the determination of the eigenfunction initial values. This method is applied to the potentials $V=x^2$, $V=x^6-bx^2$, $V=x^2+\lambda x^2/(1+gx^2)$, where exact eigenvalues are available. The numerical results, compared with the exact ones and with those of previous confirmed methods, show that the present method is accurate and efficient.

1. Introduction

The problem of the numerical computation of the eigenvalues of the one-dimensional Schrödinger equation

$$d^2y(x)/dx^2+(E-V(x))y(x)=0 \tag{1}$$

is already solved, since the early work of Cooley (1961), yet a great deal of interest for this problem is still seen, namely when the potential $V(x)$ is an even function of x.

According to the widely used Cooley (1961) shooting method, the eigenvalues E_n are determined by using the following properties of the eigenfunction:

(i) $y(x)$ and $y'(x)$ are continuous for $a\leqslant x\leqslant b$;

(ii) $y(x)$ obeys the boundary conditions

$$y(x)\underset{x\to a}{\longrightarrow}0 \qquad y(x)\underset{x\to b}{\longrightarrow}0 \tag{2}$$

where $-a=b=\infty$ for an even potential, and $a=-r_e$, $b=\infty$ for the diatomic potential with an equilibrium internuclear distance r_e (Messiah 1972).

The accuracy of this shooting method depends highly on that of the Numerov difference equation (Numerov 1933, Fröberg 1979) used to approximate equation (1). Recent works dealing with this problem seek to improve the accuracy by: (i) using higher-order difference equations (Hajj *et al* 1974, Cash and Raptis 1984, Fack and Vanden Berghe 1985, 1986, Killingbeck 1986); (ii) looking for other algorithms (Shore 1973, Mitra 1978, Kaushal 1979, Bessis and Bessis 1980, Kobeissi 1982, Fack *et al*

0305-4470/89/030287+09$02.50

1986, Cohen and Kais 1986); (iii) constructing exact solutions of (1) for specific potentials (Razavy 1980, Flessas 1981, 1982, Varma 1981, Whitehead *et al* 1982).

Within this frame, the even potential function $V(x)$ presents some particulars pointed out recently by Killingbeck (1986, 1987) and by Fack and Vanden Berghe (1987), who considered the following functions:

$$V(x) = x^z \tag{3.1}$$

$$V(x) = x^6 - bx^2 \qquad b \text{ parameter} \tag{3.2}$$

$$v(x) = x^2 + \lambda x^2/(1+gx^2) \qquad \lambda, g \text{ parameters.} \tag{3.3}$$

Each of these potentials plays a role in several areas of physics.

The aim of this work is to show that the recent 'canonical functions method' (Kobeissi 1982), already used with success for diatomic potentials (Kobeissi *et al* 1983, 1988, Dagher *et al* 1984, 1988), can be extended to symmetrical potentials. The method is 'canonical' in the sense that it dissociates the determination of the eigenvalue from that of the eigenfunction, and allows the derivation of an 'eigenvalue equation' related uniquely to the given potential $V(x)$. The theory is presented in § 2, and tested for $V(x) = x^2$ in § 3 where we underline the fact that the proposed method may be used with several difference equations. Applications to other potentials are presented in § 4 along with comparisons with previous works.

2. The eigenvalue equation

For a given potential $V(x)$ and for an arbitrary value of the 'parameter' E, the solution of (1) may be written

$$y(E; x) = y(E; x_0)\alpha(E; x_0; x) + y'(E; x_0)\beta(E; x_0; x) \tag{4}$$

where x_0 is an arbitrary origin ($a < x_0 < b$), α and β are two particular solutions of (1) having the initial values

$$\alpha(E; x_0; x_0) = \beta'(E; x_0; x_0) = 1 \qquad \alpha'(E; x_0; x_0) = \beta(E; x_0; x_0) = 0. \tag{5}$$

By imposing on $y(E; x)$ the boundary conditions at a and b, one can write

$$0 = y(E; x_0)\alpha(E; x_0; a) + y'(E; x_0)\beta(E; x_0; a) \tag{6}$$

$$0 = y(E; x_0)\alpha(E; x_0; b) + y'(E; x_0)\beta(E; x_0; b) \tag{6'}$$

and deduce the 'eigenvalue equation' (Kobeissi 1982)

$$\alpha(E; x_0; a)/\beta(E; x_0; a) - \alpha(E; x_0; b)/(E; x_0; b) = 0. \tag{7}$$

It is useful to point out that the use of the ratio

$$q(E; x_0; x) = -\alpha(E; x_0; x)/\beta(E; x_0; x) \tag{8}$$

allows one to consider the 'limits'

$$l^-(E; x_0) = \lim_{x \to a} q(E; x_0; x) \tag{9}$$

$$l^+(E; x_0) = \lim_{x \to b} q(E; x_0; x) \tag{9'}$$

and to notice that for a solution $\tilde{E}$ of (7) (where $\tilde{E}$ is an eigenvalue of (1)) and according to equations (6) and (6')

$$l^-(\tilde{E}; x_0) = l^+(\tilde{E}; x_0) = y'(\tilde{E}; x_0)/y(\tilde{E}; x_0). \tag{10}$$

More generally, we associate with the potential $V(x)$, the 'eigenvalue function' $F(E)$ defined by

$$F(E) = l^+(E; x_0) - l^-(E; x_0) \tag{11}$$

and having for zeros the solutions of (7), i.e. the eigenvalues $E_0, E_1, E_2, \ldots, E_n, \ldots$ related to the given potential $V(x)$.

The 'eigenvalue equation' $F(E) = 0$ may be used for any given potential; its solutions are independent of the arbitrary 'origin' x_0. Yet when the potential $V(x)$ is symmetrical, $b = -a$, and when $x_0 = 0$, equation (7) becomes an identity for any value of E (eigenvalue or not).

Thus for a given symmetrical potential $V(x)$, one must take $x_0 \neq 0$. However, when one prefers the use of $x_0 = 0$ for practical or theoretical reasons, a different formulation of the eigenvalue equation may be derived as follows.

For a symmetrical potential, and for $x_0 = 0$, the eigenfunction $y_n(x) = y(E_n; x)$ has initial values at $x_0 = 0$ depending on the parity of n, i.e.

$$y(E_{n'}; 0) \neq 0 \qquad y'(E_{n'}; 0) = 0 \qquad n' \text{ even} \tag{12}$$

$$y(E_{n''}; 0) = 0 \qquad y'(E_{n''}; 0) \neq 0 \qquad n'' \text{ odd.} \tag{12'}$$

When we impose the boundary condition at a (or at b), we obtain according to the parity of n

$$y(E_{n'}; a) = 0 = y'(E_{n'}; 0)\alpha(E_{n'}; 0; a)$$

or

$$y(E_{n''}; a) = 0 = y'(E_{n''}; 0)\beta(E_{n''}; 0; a)$$

and for an arbitrary value of E

$$y(E; a) = 0 = y(E; 0)\alpha(E; 0; a) + y'(E; 0)\beta(E; 0; a). \tag{13}$$

This last equation allows one to consider the logarithmic derivative of y at $x = 0$, and to write

$$\begin{aligned} l(E; 0) = y'(E; 0)/y(E; 0) &= -\alpha(E; 0; a)/\beta(E; 0; a) \\ &= -\alpha(E; 0; b)/\beta(E; 0; b). \end{aligned} \tag{14}$$

According to equations (12) and (12'), $l(E; 0)$ takes the values zero for $E = E_{n'}$ (even level), and infinity for $E = E_{n''}$ (odd level). Consequently we associate with the symmetrical potential $V(x)$ the 'eigenvalue function' $G(E) = l(E; 0)$, such as

$$G(E) = \begin{cases} 0 & \text{for even eigenvalues} \\ \infty & \text{for odd eigenvalues.} \end{cases} \tag{15}$$

The use of the 'canonical functions' $\alpha(E; x_0; x)$ and $\beta(E; x_0; x)$ allows us to derive the eigenvalue equation in its general form (equation (7) for any potential, with $x_0 \neq 0$ for an even potential), or in a form peculiar to the even potential (15).

The determination of the eigenvalue E_n being thus dissociated from that of the eigenfunction $y(E_n; x)$, one may easily deduce $y(E_n; x)$ from E_n. Once E_n is known from (7), we deduce from (6) the $y-\log$ derivative at x_0

$$y'(E; x_0)/y(E; x_0) = -\alpha(E; x_0; a)/\beta(E; x_0; a). \tag{16}$$

This relation allows one to take $y(E; x_0) = 1$ (with no loss of generality), and to deduce $y'(E; x_0)$ in terms of α and β for any E, and thus for an eigenvalue E_n.

Therefore, once E_n is known, the eigenfunction initial values are known, i.e. the eigenfunction $y(E_n; x)$ is deduced.

This general conclusion is simplified in the case of a symmetrical potential with $x_0 = 0$, where the eigenfunction $y(E_n; x)$ is nothing but one of the two canonical functions according to the parity of n (equations (4) and (8))

$$y(E_{n'}; x) = C\alpha(E_{n'}; 0; x) \qquad n' \text{ even}$$

$$y(E_{n''}; x) = C\beta(E_{n''}; 0; x) \qquad n'' \text{ odd}$$

where C is an arbitrary constant determined as usual by normalisation.

3. The harmonic oscillator

The harmonic oscillator $V(x) = x^2$ is well designed to illustrate the numerical application of the present method, and to make useful comparisons with previous works, namely with those of Killingbeck (1987) and Fack and Vanden Berghe (1985, 1987).

The determination of the eigenvalues $E_0, E_1, \ldots, E_n, \ldots$ is done by looking to the successive solutions of equation (7) when E varies from zero to infinity. The numerical application is done in the following order.

(i) We start at x_0 ($=1$, for example) to compute $\alpha(E; x_0; x)$ and $\beta(E; x_0; x)$ for $x > x_0$, by replacing (1) by a convenient difference equation (that of Numerov (1933), for example). This computation is stopped when the function $q(E; x_0; x) = -\alpha(E; x_0; x)/\beta(E; x_0; x)$ reaches a constant $l^+(E; x_0)$ (within a precision ε) for a value $x^+(E)$. This is the numerical value of b.

(ii) Step (i) is repeated for $x < x_0$; $l^-(E; x_0)$ and $x^-(E)$ are obtained.

(iii) The function $F(E) = l^+(E; x_0) - l^-(E; x_0)$ is considered. If $F(E) = 0$ (i.e. $|F(E)| \leqslant \varepsilon$, ε being a desired tolerance or the computer precision), this value of E is an eigenvalue; if not, E is increased till we have $F(E) = 0$.

(iv) Steps (i)-(iii) are repeated for the next eigenvalue, and so on.

We show in figure 1 the variation of the function $F(E)$ with E. The shape of this curve shows that the numerical determination of its zeros $E_0, E_1, \ldots, E_n, \ldots$ (the eigenvalues of equation (1)) is easy, by using one of the well known standard techniques. The values of E_n, obtained for $n = 0, 1, 2, 3$, are given in table 1, along with those found by Fack and Vanden Berghe (1987) using the Numerov difference equation.

Our results are given by using the Numerov difference equation (with the same mesh size $h = 0.05$ used by Fack and Vanden Berghe (1987)). We verified by using other 'origins' $x_0 \neq 0$, that our results are, as must be, independent of x_0.

This work was repeated by taking $x_0 = 0$ and using the corresponding eigenvalue equation (15). We show in figure 2 the variation of $G(E)$ with E. According to (15), the zeros of this curve give the odd eigenvalues; the abscissae of the asymptotes are the even eigenvalues. The numerical results are identical to those obtained by (7) and

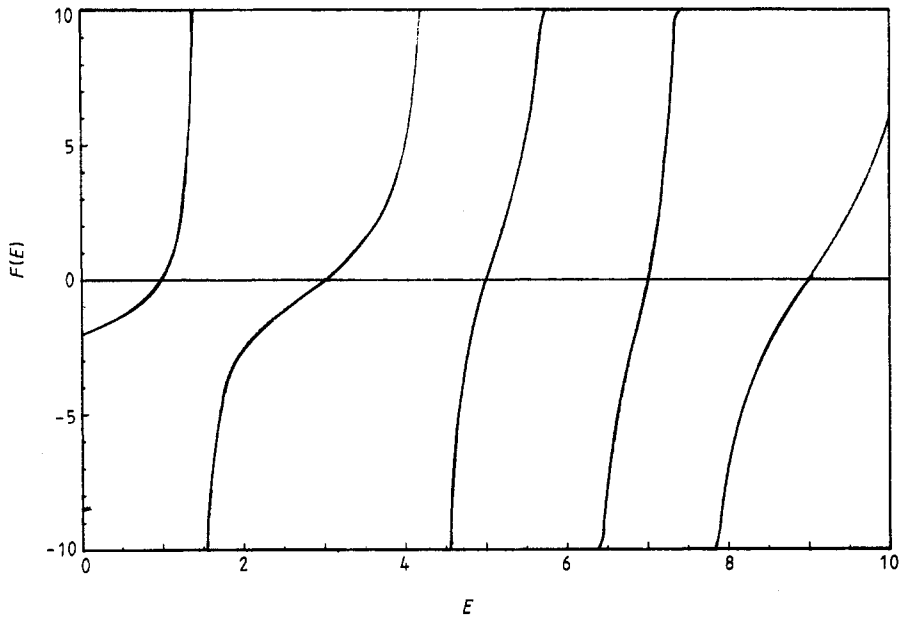

Figure 1. Variation of $F(E)$ with E.

Table 1. Comparison of the eigenvalues computed for the potential $V = x^2$, by the present method (PM), and by Fack and Vanden Berghe (1987) (FV) (for the first four levels, $0 \leqslant n \leqslant 3$). ΔE is the difference between exact and computed eigenvalues in absolute value. The two methods make use of the Numerov difference equation with a step length $h = 0.05$. R designates the total range of integration.

n	E (exact)	ΔE_{FV}	ΔE_{PM}	R_{FV}	R_{PM}
0	1	5×10^{-8}	5×10^{-9}	10	5.1
1	3	3×10^{-7}	4×10^{-8}	10	5.9
2	5	1×10^{-6}	2×10^{-7}	10	6.1
3	7	3×10^{-6}	2×10^{-7}	10	6.1

given in table 1. All computations are done on the computer HP 9000/220 (to 15 significant digits).

4. Discussion

The results of table 1 show that by using the canonical functions method with the same difference equation (Numerov) and the same mesh size ($h = 0.05$) used by Fack and Vanden Berghe (1987), the eigenvalues obtained by the present method are more accurate than those obtained by the previous one. We note also that the total range of integration R has to be determined by a prior guess for the previous work, but not for the present one; it is obtained when the ratio $q(E; x_0; x) = -\alpha(E; x_0; x)/\beta(E; x_0; x)$ reaches its asymptote $l(E; x_0)$ as $x \to +\infty$ (and/or as $x \to -\infty$). For a given potential, R is obviously a function of E and of the computation of α and β, i.e. of the numerical integration of (1).

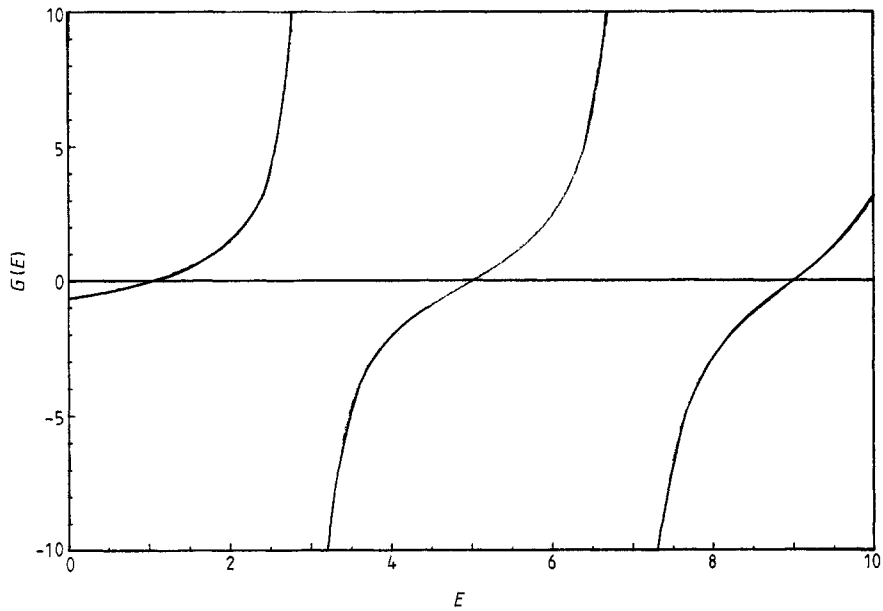

Figure 2. Variation of $G(E)$ with E.

The same remarks can be made for other potentials. We give in table 2 the results obtained for two potentials $V=-bx^2+x^6$ and $V=x^2+\lambda x^2/(1+gx^2)$ used by Fack and Vanden Berghe (1987) and for several values of the parameters. Some other applications gave similar results.

One of the major difficulties related to the present problem lies in the instability observed near the boundaries a and/or b. Several authors (Holt 1964, Osborne 1969,

Table 2. Comparison of the eignvalues computed for two potentials $V=-bx^2+x^6$ and $V=x^2+\lambda x^2/(1+gx^2)$ by the present method (PM), and by Fack and Vanden Berghe (1987) (FV) (for several values of the parameters b and λ, g). ΔE is the difference between exact and computed eigenvalues in absolute value. The two methods make use of the Numerov difference equation with the same step length h, and with the total range of integration R.

Parameter	E (exact)	ΔE_{FV}	ΔE_{PM}	R_{FV}	R_{PM}
$V=-bx^2+x^6$; $h=0.02$					
$b=11$	-8	3×10^{-7}	2×10^{-8}	4	2.8
	8	3×10^{-6}	1×10^{-6}	4	2.9
$b=13$	$-11.313\,708\,500$	5×10^{-7}	2×10^{-7}	4	2.9
	$11.313\,708\,500$	7×10^{-6}	5×10^{-7}	4	2.9
$b=15$	$-15.077\,508\,510$	5×10^{-7}	9×10^{-8}	4	3.0
	$15.077\,508\,510$	1×10^{-5}	1×10^{-6}	4	2.9
$b=17$	$-19.158\,416\,010$	6×10^{-7}	1×10^{-7}	4	2.9
	$19.158\,416\,010$	3×10^{-5}	2×10^{-6}	4	2.9
$V=x^2+\lambda x^2/(1+gx^2)$; $h=0.05$, $g=0.1$					
$\lambda=-0.42$	0.8	3×10^{-8}	1×10^{-9}	10	5.7
$\lambda=-0.67+0.1\sqrt{3.05}$	$2.3+\sqrt{3.05}$	7×10^{-7}	7×10^{-8}	10	6.1
$\lambda=-0.46$	2.4	2×10^{-7}	2×10^{-10}	10	5.9
$\lambda=-0.73+0.1\sqrt{4.09}$	$3.7+\sqrt{4.09}$	2×10^{-6}	3×10^{-9}	10	6.3

Roberts and Shipman 1971, Gupta and Agarwal 1985) pointed out that simple shooting methods applied to $V=x^2$, $E=-1$ and $x_0=0$, do not suffice to find $y(x)$ beyond $x\sim 3.5$. Killingbeck (1987) presented new techniques allowing him to reach $x\sim 5$.

We applied the present method to this specific problem, by using the Numerov difference equation with the same mesh size $h=0.05$ used by Killingbeck. We give in table 3 the values of $y(x)$ computed by our method along with those given by Killingbeck (i) by using a 'simple' shooting method and (ii) by using a 'stabilised' method. We notice that our results are even more stable than those of Killingbeck.

Table 3. Value of the solution $y(x)$ of the Schrödinger equation for $V=x^2$ and $E=-1$. For each x, the result obtained by the present method is compared with those given by Killingbeck (1987) using both a simple shooting method and a 'stabilised' one. The three methods make use of the Numerov difference equation with a step length $h=0.05$ for the two last columns and $h=0.025$ for the first one. In the last line the initial y derivative $G=y'(0)$ is deduced from each method.

x	Simple method	Stabilised method	Present method
0	1	1	1
1	0.259 344	0.259 342 6	0.259 342 547
2	0.034 566	0.034 564 1	0.034 564 045
3	0.001 992	0.001 988 5	0.001 988 523
4	0.000 157	0.000 046 0	0.000 045 958
4.5	0.000 929	0.000 004 87	0.000 004 907
5	0†	0†	0.000 000 414
5.5			0.000 000 039
G	−1.128 463	−1.128 378	−1.128 379 287

† Rendered formally zero by choice of weighting factors.

For the present problem, and for similar problems, one should distinguish between the 'method' (how to make the link between initial values and boundary conditions), and the 'tool' (how to make the numerical integration of the Schrödinger equation). The most used method, the Cooley shooting method, is usually associated with the Numerov difference equation.

However, many methods (like the canonical functions one) may be used with different 'tools'. We recently made a comparison (Kobeissi *et al* 1988) of several difference equations used for the diatomic eigenvalue problem.

The accuracy of a method depends, obviously, on the difference equation used, but also on other factors. We believe it is important, when possible, to compare two methods using the same difference equation (in order to test the 'method'), or to compare the same method using two different difference equations (in order to test the 'tool').

For this reason the examples of the numerical application presented here are done with the commonly used Numerov difference equation. Yet, the present method is shown to be efficient by using other difference equations, such as the 'integrals superposition' which is well suited for the present problem (Kobeissi 1982, Dagher *et al* 1988, Kobeissi *et al* 1988). We give in table 4 an example of our results for $V=x^2$, compared with the results obtained by Fack and Vanden Berghe (1987) with higher-order difference equations. The numerical details may be found elsewhere (Dagher *et al* 1988, Kobeissi *et al* 1988).

Table 4. Comparison of the eignevalues computed for the potential $V = x^2$ by the present method with the 'integral superposition' difference equation (last column), with those obtained by Fack and Vanden Berghe (1987) using two higher-order difference equations (for the same level n of table 1). ΔE is the difference between exact and computed eigenvalues in absolute value. The step length h and the total range R of integration are displayed for each method.

		Fack and Vanden Berghe[a]		Present method[b]
n	E (exact)	Heptadiagonal	Extended Numerov	Integrals superposition
0	1	2×10^{-10}	6×10^{-11}	2×10^{-12}
1	3	2×10^{-9}	5×10^{-10}	7×10^{-11}
2	5	7×10^{-9}	2×10^{-9}	7×10^{-11}
3	7	2×10^{-8}	7×10^{-9}	3×10^{-10}

[a] $h = 0.05$; $R = 10$.
[b] $h = 0.5$; R varies from 7 to 9.

5. Conclusion

The canonical functions formulation already used to derive an 'eigenvalue function' $F(E)$ associated with a diatomic potential (unsymmetrical one) is shown to be appropriate, under one restriction, to find the eigenvalues related to a symmetrical potential. The eigenvalues are the successive roots of the equation $F(E) = 0$; this equation depends on the 'canonical functions' α and β, well defined for the given potential, and *not* on the eigenfunction $y(x)$.

A similar formulation taking for 'origin' $x = 0$, makes use of another 'similar eigenvalue function' $G(E)$ associated with a symmetrical potential. It is proved, theoretically, that (i) the even-parity eigenvalues are obtained from $G(E) = 0$ and (ii) the odd-parity eigenvalues are obtained from $G(E) = \infty$. This last theoretical result was already mentioned by Killingbeck (1987) as a revelation of the 'computer experiment'.

The present method was applied to some potentials where exact eigenvalues are available. The comparison of the results with the exact values on one hand, and with results of other confirmed methods on the other hand, show the accuracy and the efficiency of the present method.

Acknowledgment

We are grateful to Mr I Serhal for his help during the preparation of the manuscript.

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