J. Phys. A: Math. Gen. 21 (1988) 3903-3919. Printed in the UK

Studies on algebraic methods to solve linear eigenvalue problems: generalised anharmonic oscillators

H Taşeli and M Demiralp

Applied Mathematics Department, TÜBITAK, Research Institute for Basic Sciences, PO Box 74, 41470 Gebze-Kocaeli, Turkey

Received 4 January 1988, in final form 18 May 1988

Abstract. A detailed presentation of the recently introduced integration-free method, with applications to determine the energy levels of the generalised quantum anharmonic oscillators, are given. Numerical calculations are realised for the quartic and the sextic oscillators. Energy eigenvalues obtained for the ground state as well as for the first few excited states accurate to thirty digits are very impressive and demonstrate the efficiency of the method. Certain remarks about the selection of the basis functions and a convergence discussion on the presented simple approximation scheme are also included in this paper.

1. Introduction

Almost all of the bound-state investigations of the systems encountered in quantum physics can be interpreted as eigenvalue problems of certain linear operators whose domains cover a Hilbert space. It is well known that, if only the non-relativistic case is under consideration, the Schrödinger operator characterises the system. For an atomic or molecular system, discrete and continuous spectra exist together and bound states have various accumulation points in or at the border of the continuous spectrum. The determination of such eigenvalues is a difficult problem, and almost all methods either fail or show weak convergence properties. However, the ground or low-lying states do not create such difficulties if they are sufficiently far from the starting point of the continuum. This statement is, of course, not general since it is true only if the operator is semibounded.

On the other hand, some quantum mechanical problems in crystal physics or in solid state theory generally deal with systems which possess solely discrete spectra; for example, well potentials and anharmonic oscillators. However, although the non-existence of the continuous spectrum is an important simplification, there may be some adjacent eigenvalues, numerical evaluations of which result in serious problems. The discrete and continuous parts of the spectrum of a given linear operator have different uses in practical applications. Indeed, if we are interested in the discrete spectrum the determination of the spectral points is necessary since they give the energetic structure of the system in question. In the case of continuous spectra, however, the problem characterises a scattering or a collision phenomenon, and so perhaps only the endpoint of the continuous spectrum and density of the spectral points are of importance. Thus the determination of the wavefunction is more important.

Now, if one desires to find the discrete spectrum of the Schrödinger operator of a given system, the conventional way is to convert this eigenvalue problem to a matrix

0305-4470/88/203903+17$02.50

eigenvalue problem via the selection of a basis set which spans the domain of the operator. If the basis set employed in this procedure is orthonormal, the resulting matrix eigenvalue problem is then symmetric and unit-matrix weighted. Otherwise a generalised matrix eigenvalue problem is encountered. To evaluate the elements of the matrices in the matrix representation of the Schrödinger operator and the unit operator, it is necessary to perform certain integrals. Perturbational [1-3] and variational methods may be recalled as examples. The solution of the matrix eigenvalue problem mentioned above depends completely on these integrals. The presence of integration in such methods causes two limitations. First, the trial functions have to be chosen in such a way that the integrals can be evaluated easily and, preferably, analytically. In many cases, this makes it impossible to use well defined basis functions that characterise the true behaviour of a system at the singular points of the differential operator. Second, there are serious problems due especially to the accumulation of errors when numerical integration techniques are tried. It should be noted that many methods, such as collocation and finite differences, seem to be integration-free; but, in fact, they do not remove the non-local behaviour, which is peculiar to integration in the solution technique. That is, such methods have a hidden integration character. Hence the establishment of an integration-free algorithm, which uses mostly local information, is of considerable importance in many circumstances.

It is well known that dividing the general Schrödinger equation $H\Psi = E\Psi$ by Ψ yields

$$E = H\Psi/\Psi \tag{1.1}$$

which is constant for each point in the domain of the wavefunction. Therefore, energy may be locally evaluated at any point in the domain if the exact wavefunction is known. Indeed, Bartlett [4] has pointed out that for an exact solution E is a constant whereas an approximate wavefunction or a trial function, Ψ_T, will lead to a local energy, say μ, calculated from $H\Psi_T/\Psi_T$ as a varying function of position. Bartlett used this property of local energy to test the goodness of a numerically calculated wavefunction for helium [5]. It is clear that the constancy of $H\Psi_T/\Psi_T$ can be employed at least as a criterion of the excellence of the trial function. Frost *et al* [6] have developed a least-squares method and made use of the criterion of constant energy to improve the original approximating function. Their approach, however, has a global nature.

A very different strategy is developed here, however, where the constancy of $H\Psi/\Psi$ is directly used for the construction of a new algebraic method. Our approach employs the vanishing derivatives of the ratio $H\Psi/\Psi$ as the basic idea of the method. In other words, a truncated Taylor series expansion around an internal point of the domain should have zero coefficients, except for the first constant one. So this method is of a completely local character.

In this paper we show how an integration-free method, the main outlines of which have been introduced by Demiralp [7], can be developed to solve linear eigenvalue problems. The formalism of the method is given in § 2. In § 3, generalised anharmonic oscillators are briefly reviewed and a novel trial function is constructed in such a way that it reflects the particular behaviour of the exact wavefunction. Subsections 3.1 and 3.2 cover the particular cases of the quartic and sextic oscillators. Extremely accurate numerical results are presented in § 4 in the entire range of the anharmonicity constant. The last section includes a convergence discussion of the algorithm and some concluding remarks.

2. The Wronskian approach

Let us consider the following eigenvalue problem:

$$\mathscr{L}\Psi = \lambda\Psi \qquad \Psi \in \mathscr{D}(\mathscr{L}) \subset \mathscr{H} \tag{2.1}$$

where $\mathscr{L}$ denotes a linear ordinary differential operator whose domain, $\mathscr{D}(\mathscr{L})$, is a subspace of a Hilbert space, $\mathscr{H}$. We have assumed, without any loss of generality, that $\mathscr{L}$ contains only one independent variable. Indeed, all conceptual features of the scheme remain unchanged when it is extended to the many-dimensional case. We also assume that $\mathscr{L}$ has only a discrete spectrum, in order to avoid the aforementioned difficulties of the continuous spectrum.

Let us now choose a trial function, Ψ_T, for the approximate solution of (2.1):

$$\Psi_T(x) = \sum_{j=1}^{N} c_j\phi_j(x) \tag{2.2}$$

and consider the ratio

$$\mu(x) = \mathscr{L}\Psi_T(x)/\Psi_T(x) \tag{2.3}$$

where x stands for the independent variable and the ϕ_j are the elements of a basis set which spans the domain of the operator. If $\Psi_T(x)$ were a true eigenfunction of $\mathscr{L}$, the ratio would be a constant equal to the corresponding eigenvalue on the entire interval of x. Otherwise, it is evident that $\mu(x)$ is a function of x. The construction of a basis set such that $\{\phi_j(x): j = 1, 2, \ldots\}$ and $\{\mathscr{L}\phi_j(x) \equiv u_j(x): j = 1, 2, \ldots\}$ satisfy the accompanying boundary conditions of (2.1) is, however, possible in order to make $\mu(x)$ finite everywhere. Furthermore, since a constant function is infinitely differentiable and all derivatives are zero, we can impose the following $(N-1)$ conditions on $\mu(x)$ by assuming that the ϕ_j are infinitely differentiable:

$$\{D^k\mu(x)\}_{x=x_0} = 0 \qquad D^k \equiv \mathrm{d}^k/\mathrm{d}x^k \qquad k = 1, 2, \ldots, N-1. \tag{2.4}$$

This is equivalent to equating to zero the first $(N-1)$ derivatives of the Taylor expansion of $\mu(x)$ at a specific point, x_0. That is,

$$\mu(x) = \mu(x_0) + \mathrm{O}((x-x_0)^N) \tag{2.5}$$

which means that $\mu(x)$ is almost a constant function in a sub-interval centred at x_0. The extra condition on $\mathscr{L}\Psi_T$ is due to the fact that if $\mathscr{L}\Psi_T$ does not satisfy the boundary conditions then $\mu(x)$ goes to infinity at the boundary points of the x interval. This is, of course, an undesired property since in this way the flatness of $\mu(x)$ is affected in an important area.

Now, if we differentiate both side of (2.3), $\mathscr{L}\Psi_T(x) = \mu(x)\Psi_T(x)$, in conjunction with (2.2), up to $(N-1)$th order

$$\sum_{j=1}^{N} c_j\{D^{k-1}u_j(x)\}_{x=x_0} = \sum_{j=1}^{N} c_j \sum_{l=0}^{k-1} \binom{k-1}{l} \{[D^l\mu(x)][D^{k-1-l}\phi_j(x)]\}_{x=x_0} \tag{2.6}$$

$$D^0 \equiv 1 \qquad k = 1, 2, \ldots, N \tag{2.7}$$

and take into account the conditions expressed in (2.4),

$$\sum_{j=1}^{N} c_j\{D^{k-1}u_j(x)\}_{x=x_0} = \mu(x_0) \sum_{j=1}^{N} c_j\{D^{k-1}\phi_j(x)\}_{x=x_0} \tag{2.8}$$

from which we arrive at the generalised matrix eigenvalue problem:

$$\sum_{j=1}^{N} (\mathscr{A}_{kj} - \lambda \mathscr{B}_{kj}) c_j = 0 \qquad k = 1, 2, \ldots, N \tag{2.9}$$

where the elements of the matrices $\mathscr{A}$ and $\mathscr{B}$ are defined as

$$\mathscr{A}_{kj} \equiv \{D^{k-1} u_j(x)\}_{x=x_0} \tag{2.10}$$

and

$$\mathscr{B}_{kj} \equiv \{D^{k-1} \phi_j(x)\}_{x=x_0} \tag{2.11}$$

respectively, and λ

$$\lambda \equiv \mu(x_0) \tag{2.12}$$

represents the approximate eigenvalue in question. Therefore, we obtain

$$\mathscr{A} c = \lambda \mathscr{B} c \tag{2.13}$$

in vector-matrix notation, where

$$c^{\mathrm{T}} = [c_1, c_2, \ldots, c_N]. \tag{2.14}$$

$\mathscr{B}$ and $\mathscr{A}$ are the Wronskian matrices of the set $\{\phi_j(x)\}$ and the transformed set $\{u_j(x)\}$ respectively, so that this scheme may be called the 'Wronskian approach'. The generalised eigenvalue problem (2.13) may yield complex pairs of eigenvalues depending on the x_0 value and the nature of $\mathscr{L}$ and $\{\phi_j\}$ due to the non-symmetric structure of $\mathscr{A}$ and $\mathscr{B}$. We may conjecture, however, that it is possible to find certain x_0 values for which a real λ can be obtained. It is also possible to convert $\mathscr{B}$ into the identity matrix by a convenient selection of the ϕ_j. These arguments will become clearer in the following sections when the method is applied to solve specific problems. Above all, if the ϕ_j form a complete set one can expect that the scheme converges as N goes to infinity. However, we leave the convergence proof to future studies.

3. Generalised anharmonic oscillators

The quantum mechanical description of generalised anharmonic oscillators in the one-dimensional case is given by the Schrödinger equation

$$H\Psi(x) = E\Psi(x) \qquad x \in (-\infty, \infty) \tag{3.1}$$

$$H = -\mathrm{d}^2/\mathrm{d}x^2 + x^2 + \beta x^{2m} \qquad m = 2, 3, \ldots \qquad \beta \geqslant 0 \qquad E = E(m, \beta) \tag{3.2}$$

with the boundary condition

$$\lim_{x \to \pm\infty} \Psi(x) = 0 \tag{3.3}$$

where $\Psi(x)$, E and β are the wavefunction, energy eigenvalue and anharmonicity constant, respectively. With the introduction of a scaling parameter, ν, and the transformation of the variable x to $\nu^{1/2}x$, the equation becomes

$$[-\mathrm{d}^2/\mathrm{d}x^2 + \nu^2 x^2 + (1 - \nu^{m+1}) x^{2m}]\Psi(x) = \nu E \Psi(x) \tag{3.4}$$

where the scaling parameter is defined by

$$\nu = (1+\beta)^{-1/(m+1)} \qquad 0 \leqslant \nu \leqslant 1 \tag{3.5}$$

in order to obtain a bounded potential for all regimes of the anharmonicity constant.

A review of the anharmonic oscillators problem is outside the scope of this work. Our aim is merely to test the Wronskian approach. We may, however, outline the main approaches in three groups: perturbative methods [8-11] which emphasise the resummation of the divergent Rayleigh-Schrödinger series; non-perturbative methods which try to obtain the best approximate wavefunction by variational techniques [12-14], iterative techniques [15] or by a characteristic function algorithm [16-18]; and the method of the Hill determinant [19-21]. As is well known, all these methods are equally useful depending on their particular limitations.

Let us now examine the mathematical structure of the Hamiltonian (3.2). First, H is positive definite as long as β is non-negative. The positive definiteness and the self-adjointness of the operator implies that it possesses a real positive and discrete spectrum. It is well known that the spectral points of the harmonic oscillator are equally spaced, whereas in the case of the anharmonic oscillators discussed here, as the state number and the parameter β increase, the difference between any two consecutive eigenlevels is broadened. That is, none of the eigenvalues of H are close to each other, so the spectrum is numerically well isolated. Another property of H is that the non-existence of odd terms in x makes it possible to separate the set of eigenlevels into two subsets which contain even and odd functions of x, respectively, i.e. symmetric and antisymmetric levels.

On the other hand, the wavefunction is square integrable over the entire real axis of the x-complex plane due to the discrete character of the spectrum and the accompanying boundary conditions (3.3) of the problem. Thus the approximate wavefunction (in other words the trial function, Ψ_T) must decay exponentially when x goes to infinity, in order to compensate the irregular singular behaviour of H at infinity. The structure of the argument of this exponential factor depends on the anharmonicity constant β and the number m. It is $-x^2/2$ for the harmonic oscillator when $\beta = 0$. However, a function of the absolute value of x, the dominant term of which is proportional to $|x|^3$ [22], should be used in the case of the quartic oscillator where $m = 2$. The determination of the exponential factor can be accomplished by making use of the condition

$$\lim_{x \to \pm\infty} H\Psi_T/\Psi_T = \text{constant}. \tag{3.6}$$

This condition is automatically fulfilled if the exact wavefunction is known. However, when we have an approximate wavefunction, Ψ_T, the necessary and sufficient condition for $H\Psi_T$ to be contained in the space to which Ψ_T belongs is (3.6). Then, $H\Psi_T$ is also in the space of the square integrable functions, L_2. It is evident that the exact wavefunction satisfies the relation

$$H^n\Psi/\Psi = E^n \qquad H^n\Psi \in L_2 \qquad H^0 = 1 \qquad n = 0, 1, \ldots \tag{3.7}$$

for the entire interval of x, $x \in (-\infty, \infty)$. Hence, enforcing the trial function to satisfy the conditions at the singular points of H

$$\lim_{x \to \pm\infty} H^n\Psi_T/\Psi_T = \text{constant} \qquad n = 1, 2, \ldots \tag{3.8}$$

is of considerable importance. Since there is no singularity in any finite subregion of the x-complex plane, the Frobenius theory of ordinary differential equations dictates that two linearly independent solutions of (3.4) can be expanded into Maclaurin series, both of which are multiplied by an exponential function. Such solutions coverge in all circles centred at the origin whose radii are finite. On the contrary, if we wish to find solutions of (3.4) which are valid for large values of x, we then seek solutions in

the form of infinite series with variable $1/x$. These serial expansions in inverse powers of x are divergent but asymptotic due to the irregular singularity of 'the point at infinity'. Therefore, it seems almost impossible to obtain an analytic continuation by appropriate manipulations on the power series.

All these discussions will be taken into consideration for the selection of the trial function. It is noteworthy that the integration-free character of the Wronskian approach enables us to employ complicated basis functions without any problem. First, let us consider the coordinate transformation

$$\xi = (1+\alpha x^2)^{-1/p} \qquad \xi \in [0, 1]. \tag{3.9}$$

There are three reasons for introducing a new variable ξ. Firstly, since ξ is an even function of x we can deal only with the symmetric states of H. This specification, in fact, does not create any loss of generality, because a similar procedure holds to determine the antisymmetric states of H when $\Psi(x)$ is replaced by $x\Psi(x)$ in (3.4). Secondly, if one is interested in the symmetric states of (3.4), the expansion of the wavefunction at the origin of the x axis is expressible as

$$\Psi(x) = 1 + c_2 x^2 + c_4 x^4 + \dots . \tag{3.10}$$

However, imitating this behaviour of the exact wavefunction is extremely difficult due to the dependence on the absolute value of x in the argument of the necessary exponential function mentioned above. Making use of ξ, an expansion in terms of x for the approximate wavefunction of the form (3.10) can be obtained provided that

$$p = \begin{cases} 2 & \text{for even } m \\ 1 & \text{for odd } m. \end{cases} \tag{3.11}$$

Thirdly, the insertion of an arbitrary parameter, α, yields a flexibility to accelerate the convergence of the algorithm.

Therefore the problem of determining the symmetric eigenvalues of (3.4) is converted to

$$H_m \Psi(\xi) = \tfrac{1}{4} p^2 \nu E(m, \beta) \Psi(\xi) \tag{3.12}$$

$$H_m = \alpha(\xi^p - 1)\xi^{p+2} \, \mathrm{d}^2/\mathrm{d}\xi^2 + \alpha[(p+1)(\xi^p - 1) + \tfrac{1}{2}p]\xi^{p+1} \, \mathrm{d}/\mathrm{d}\xi + V(\xi) \tag{3.13}$$

$$V(\xi) = \tfrac{1}{4} p^2 [(\xi^{-p} - 1)\nu^2/\alpha + (\xi^{-p} - 1)^m (1 - \nu^{m+1})/\alpha^m] \tag{3.14}$$

by the change of variable from x to ξ.

With the general outline of constructing the basis functions in perspective, we can now choose a trial function of the form

$$\Psi_T(\xi) = f(\xi) \exp[g(\xi)] \tag{3.15}$$

$$f(\xi) = \sum_{j=1}^{\infty} f_j (-p/\alpha)^{j-1} (\xi - 1)^{j-1} \qquad f_1 = 1 \tag{3.16}$$

where the f_j are the unknown coefficients in the linear combination and $g(x)$ is the function which is to be determined by utilising the condition expressed in (3.6). Consequently, it is shown that the trial function reflects the asymptotic behaviour of the exact wavefunction at infinity. Furthermore, if we consider the limiting case of ξ, when ξ goes to one or, equivalently, when x goes to zero

$$\xi \approx 1 + (-\alpha/p)x^2 + \dots \qquad x^2 \approx (-p/\alpha)(\xi - 1) + \dots \tag{3.17}$$

then Ψ_T can be regularly expanded for sufficiently small values of x similar to (3.10).

3.1. The quartic oscillator

The most studied system of general anharmonic oscillators is the quartic anharmonic oscillator. In this case, for which $m=2$ and $p=2$, we have

$$H_2\Psi(\xi)=\nu E(2,\beta)\Psi(\xi) \tag{3.18}$$

$$H_2=\alpha(\xi^2-1)\xi^4\,\mathrm{d}^2/\mathrm{d}\xi^2+\alpha(3\xi^2-2)\xi^3\,\mathrm{d}/\mathrm{d}\xi + \nu^2(\xi^{-2}-1)/\alpha+(1-\nu^3)(\xi^{-2}-1)/\alpha^2 \tag{3.19}$$

$$\nu=(1+\beta)^{-1/3}. \tag{3.20}$$

From the aforementioned considerations, the trial function may be written in the form

$$\Psi_T(\xi)=f(\xi)\exp(-\tfrac{1}{3}a_2\xi^{-3}+a_1\xi^{-1}+a_0\ln\xi) \qquad a_2>0 \tag{3.21}$$

from which it follows that

$$\frac{H_2\Psi_T(\xi)}{\Psi_T(\xi)}=\frac{Tf(\xi)}{f(\xi)}+\frac{1}{\alpha^2}\{(1-\nu^3-\alpha^3a_2^2)\xi^{-4} +[2\alpha^3a_1a_2+\alpha^3a_2^2-2(1-\nu^3)+\alpha\nu^2]\xi^{-2}+2\alpha^3a_2(1-a_0)\xi^{-1}\}. \tag{3.22}$$

The condition (3.6) evidently implies

$$\alpha^3a_2^2-(1-\nu^3)=0 \tag{3.23}$$

$$2\alpha^{3/2}(1-\nu^3)^{1/2}a_1-(1-\nu^3)+\alpha\nu^2=0 \tag{3.24}$$

$$a_0-1=0 \tag{3.25}$$

for the determination of the parameters, a_0, a_1 and a_2. Thus the problem is altered to

$$Tf(\xi)=\nu E(2,\beta)f(\xi) \tag{3.26}$$

where the operator T is

$$T=\alpha\xi^4(\xi^2-1)\,\mathrm{d}^2/\mathrm{d}\xi^2+\alpha[5\xi^5-2a_1\xi^4-4\xi^3+2(a_1+a_2)\xi^2-2a_2]\,\mathrm{d}/\mathrm{d}\xi +\alpha[3\xi^4-3a_1\xi^3+(a_1^2-2)\xi^2+(2a_1+a_2)\xi-a_1^2]. \tag{3.27}$$

It is not difficult to prove that the ratio $H^n\Psi_T/\Psi_T$, for $n=2,3,\ldots$, tends to a constant as $|x|\to\infty$ or $\xi=0$ when the requirement for the constancy of $H\Psi_T/\Psi_T$ is realised. That is, the conditions expressed in (3.8) are automatically fulfilled.

We can now construct the Wronskian matrices in order to evaluate the approximate eigenvalues of the problem. From (3.16) we have

$$f(\xi)=\sum_{j=1}^{\infty}f_j(-\tfrac{1}{2}\alpha)^{j-1}(\xi-1)^{j-1} \tag{3.28}$$

and with the definitions (2.10) and (2.11) we may derive the elements of the matrices in the forms

$$\mathscr{B}_{kj}=(-\tfrac{1}{2}\alpha)^{k-j}[D^{k-1}(\xi-1)^{j-1}]_{\xi=1}/(k-1)!=\delta_{kj} \tag{3.29}$$

and

$$\begin{aligned}\mathscr{A}_{kj} &= (-\tfrac{1}{2}\alpha)^{k-j}[D^{k-1}T(\xi-1)^{j-1}]_{\xi=1}/(k-1)! \\ &= \tfrac{1}{16}\alpha^5[(j-1)(j-2)+5(j-1)+3]\delta_{k,j+4} \\ &\quad -\tfrac{1}{8}\alpha^4[6(j-1)(j-2)+(25-2a_1)(j-1)+3(4-a_1)]\delta_{k,j+3} \\ &\quad +\tfrac{1}{4}\alpha^3[14(j-1)(j-2)+2(23-4a_1)(j-1)+(a_1-3)(a_1-6)-2]\delta_{k,j+2} \\ &\quad -\tfrac{1}{2}\alpha^2[16(j-1)(j-2)+2(19-5a_1+a_2)(j-1) \\ &\quad +(2a_1+1)(a_1-4)+a_2+12]\delta_{k,j+1} \\ &\quad +\alpha[9(j-1)(j-2)+(13-4a_1+4a_2)(j-1)+(1-a_1+a_2)]\delta_{k,j} \\ &\quad -2(2j-3)(j-1)\delta_{k,j-1}. \end{aligned} \tag{3.30}$$

The matrix $\mathscr{A}$ so defined reduces to the identity matrix. The harmonic oscillator is a special case of the problem. Equation (3.23) implies that the parameter α is zero when $\beta=0$ or $\nu=1$, where

$$\mathscr{A}_{kj} = [4\alpha(a_2-a_1)(j-1)+\alpha(a_2-a_1)]\delta_{k,j}-2(2j-3)(j-1)\delta_{k,j-1}. \tag{3.31}$$

It should also be observed that the spectrum of $\mathscr{A}$ is equal to the well known spectrum of the harmonic oscillator if

$$\alpha(a_2-a_1)=1. \tag{3.32}$$

This may be taken into account as an extra condition for the estimation of α. Therefore, the derivations of the parameters result in

$$\alpha = (1-\nu^3)/[1+(1-\nu^2)^{1/2}]^2 \tag{3.33}$$

$$a_1 = (1-\nu^2)^{1/2}/\alpha \tag{3.34}$$

$$a_2 = (1-\nu^3)^{1/2}/\alpha^{3/2}. \tag{3.35}$$

3.2. The sextic oscillator

The problem of the sextic oscillator, where $m=3$, may be worked out in a similar fashion. In this case the trial function is of the form

$$\Psi_T(\xi) = f(\xi)\exp[-\tfrac{1}{2}a_1\xi^{-1}(\tfrac{1}{2}\xi^{-1}-1)+a_0\ln\xi] \tag{3.36}$$

where

$$\xi = (1+\alpha x^2)^{-1} \tag{3.37}$$

$$f(\xi) = \sum_{j=1}^{\infty} f_j(-1/\alpha)^{j-1}(\xi-1)^{j-1}. \tag{3.38}$$

The modified eigenvalue problem can be derived as

$$Tf(\xi) = \nu E(3,\beta)f(\xi) \tag{3.39}$$

where

$$\begin{aligned} T &= 4\alpha(\xi-1)\xi^3\,\mathrm{d}^2/\mathrm{d}\xi^2+2a[4(a_0+1)\xi^3-(4a_0+2a_1+3)\xi^2+4a_1\xi-2a_1]\,\mathrm{d}/\mathrm{d}\xi \\ &\quad +2\alpha a_0[2(a_0+1)\xi^2-(2a_0+2a_1+1)\xi+2a_1] \end{aligned} \tag{3.40}$$

$$\nu = (1+\beta)^{-1/4}. \tag{3.41}$$

By our Wronskian approach the corresponding matrix eigenvalue problem is

$$\mathscr{A}f = \nu E(3,\beta)f \tag{3.42}$$

$$f^{\mathrm{T}} = [1, f_2\ f_3, \ldots] \tag{3.43}$$

where the elements of the matrix are defined by

$$\begin{aligned}\mathscr{A}_{kj} = {} & 4\alpha^3[(j-1)(j-2)+2(a_0+1)(j-1)+a_0(a_0+1)]\delta_{k,j+2} \\ & -2\alpha^2[6(j-1)(j-2)+(8a_0-2a_1+9)(j-1)+a_0(2a_0-2a_1+3)]\delta_{k,j+1} \\ & +[12\alpha(j-1)(j-2)+4(3\alpha+1)(j-1)+1]\delta_{k,j} \\ & -2(2j-3)(j-1)\delta_{k,j-1}. \end{aligned} \tag{3.44}$$

The determination of the parameters α, a_0 and a_1 is similar to that of the quartic oscillator case:

$$\alpha = 2(1-\nu^4)^{1/2}/[\nu^2+3(1-\nu^4)^{1/2}] \tag{3.45}$$

$$a_0 = 1/2\alpha \tag{3.46}$$

$$a_1 = (1-\nu^4)^{1/2}/\alpha^2. \tag{3.47}$$

As can be readily shown, the extension of the method to the octic oscillator and other systems of this kind is straightforward.

4. Numerical results

The truncated matrix eigenvalue problem

$$\sum_{j=1}^{N} [\mathscr{A}_{kj} - \nu E(m,\beta)\delta_{kj}]f_j = 0 \qquad m = 2, 3 \qquad k = 1, 2, \ldots, N \tag{4.1}$$

where N is the size of truncation, is solved for illustrative purposes. Since the matrix $\mathscr{A}$ is non-symmetric certain numerical difficulties may be expected. However, for both $m = 2$ and $m = 3$ the transpose of the Wronkian matrix, $\mathscr{A}^{\mathrm{T}}$, is of an upper Hessenberg form and of a banded structure. This simpler structure enables us to determine isolated eigenvalues accurately. Hence the QR algorithm for real Hessenberg matrices and the related package routines are employed [23]. We used quadruple precision arithmetic on a VAX-11/780 computer (34 digits) by truncating the results to 30 significant digits.

In tables 1-6 we report the ground-state and the first five symmetric excited-state energy levels of the quartic anharmonic oscillator as a function of the anharmonicity constant, β. It is apparent that the Wronskian approach yields the most accurate numerical results for the ground-state eigenvalues. A slight slowing down of convergence is observed as the state number, n, increases. For very high state numbers it is

Table 1. Ground-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_0(2,\beta)$
0.00001	6	1.000 007 499 868 755 202 823 411 051 00
0.0001	8	1.000 074 986 880 200 111 122 834 155 30
0.001	12	1.000 748 692 673 185 699 538 485 009 30
0.01	18	1.007 373 672 081 382 460 533 843 905 98
0.1	29	1.065 285 509 543 717 688 857 091 628 79
1	47	1.392 351 641 530 291 855 657 507 876 61
10	48	2.449 174 072 118 386 918 268 793 906 19
100	47	4.999 417 545 137 587 829 294 632 037 35
1000	47	10.639 788 711 328 046 063 622 042 669 4
40000	48	36.274 458 133 736 835 470 376 382 678 5

Table 2. $n = 2$ excited-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_2(2, \beta)$
0.00001	8	5.000 097 496 156 563 699 455 321 513 81
0.0001	10	5.000 974 615 938 385 599 377 851 129 58
0.001	14	5.009 711 872 788 107 487 036 992 247 36
0.01	20	5.093 939 132 742 309 225 377 304 880 23
0.1	33	5.747 959 268 833 563 304 733 503 118 48
1	57	8.655 049 957 759 309 688 116 539 457 38
10	55	16.635 921 492 413 757 783 361 917 932 2
100	54	34.873 984 261 994 777 546 412 103 561 2
1000	52	74.681 404 200 164 813 260 852 269 799 1
40000	52	255.017 677 289 573 984 846 933 213 430

Table 3. $n = 4$ excited-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_4(2, \beta)$
0.00001	10	9.000 307 479 696 423 799 458 683 180 87
0.0001	12	9.003 072 972 044 612 550 295 311 892 34
0.001	16	9.030 549 566 074 710 815 387 279 511 65
0.01	24	9.289 479 816 311 885 668 219 161 173 62
0.1	39	11.098 595 622 633 043 011 086 458 749 3
1	61	18.057 557 436 303 252 894 771 239 646 5
10	58	35.885 171 222 253 873 712 281 269 098 2
100	58	75.877 004 028 669 724 180 840 011 902 9
1000	56	162.802 374 196 975 230 178 579 711 889
40000	57	556.200 474 630 523 658 811 864 176 747

Table 4. $n = 6$ excited-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_6(2, \beta)$
0.00001	11	13.000 637 440 292 271 633 739 640 1305
0.0001	13	13.006 369 039 122 732 754 257 612 4199
0.001	18	13.063 163 577 678 484 276 559 322 2201
0.01	27	13.586 715 801 589 590 012 276 182 4546
0.1	43	16.954 794 686 144 151 337 692 616 5088
1	65	28.835 338 459 504 248 840 133 635 7155
10	64	58.241 298 739 753 240 285 104 217 6544
100	60	123.640 697 626 678 167 674 110 965 464
1000	62	265.519 951 678 280 012 371 053 662 368
40000	62	907.329 749 584 390 178 419 610 048 216

Table 5. $n = 8$ excited-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_8(2, \beta)$
0.00001	12	17.001 087 367 750 291 530 519 915 1999
0.0001	15	17.010 861 803 328 668 215 896 135 4641
0.001	20	17.107 457 792 653 472 941 979 976 5127
0.01	30	17.979 510 583 711 218 430 177 756 4069
0.1	47	23.229 552 179 939 289 070 647 087 4343
1	69	40.690 386 082 106 444 725 278 931 4816
10	69	83.003 867 037 585 290 020 430 796 0934
100	65	176.628 655 957 714 353 603 604 728 193
1000	67	379.511 311 178 728 667 693 290 769 435
40000	67	1297.030 657 027 216 185 205 102 512 01

Table 6. $n = 10$ excited-state energy eigenvalues of the quartic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_{10}(2, \beta)$
0.00001	14	21.001 657 251 878 915 214 744 230 9504
0.0001	16	21.016 550 253 042 501 755 118 151 5730
0.001	21	21.163 338 105 703 820 534 172 441 0607
0.01	33	22.462 605 642 166 157 812 716 221 4995
0.1	52	29.866 525 234 671 278 018 365 238 9140
1	72	53.449 102 139 665 264 600 831 506 4598
10	72	109.772 570 864 332 974 973 673 879 837
100	70	233.966 225 876 235 944 863 913 218 793
1000	71	502.886 399 284 715 911 615 348 140 903
40000	72	1718.834 435 887 075 492 178 358 411 30

necessary to provide large N. However, for all values of β in the first six states, it is shown that the maximum size of truncation is 72. The truncation size, for which the desired accuracy is obtained, is also included in the tables. The accuracy of the results, which are in excellent agreement, especially with those of Banerjee [20], is checked in several ways and the maximum uncertainty in the tabulated eigenvalues is ± 1 in the last significant figure.

Numerical results for the sextic oscillator are similarly presented in tables 7–10. Results are given only for the first four states and only for four β values in order not

Table 7. Ground-state energy eigenvalues of the sextic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_0(3, \beta)$
0.00001	37	1.000 018 747 270 740 851 501 269 085 99
10	83	2.205 723 269 595 632 351 009 973 387 17
1000	80	6.492 350 132 329 671 550 549 557 845 32
40000	80	16.211 718 264 749 243 619 248 517 555 9

Table 8. $n = 2$ excited-state energy eigenvalues of the sextic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_2(3, \beta)$
0.00001	40	5.000 468 519 726 976 688 596 974 561 75
10	86	16.641 218 108 251 080 173 659 025 662 6
1000	86	51.182 480 106 305 690 884 693 028 921 5
40000	87	128.376 742 015 189 214 870 771 197 740

Table 9. $n = 4$ excited-state energy eigenvalues of the sextic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_4(3, \beta)$
0.00001	42	9.002 415 883 909 077 122 103 173 565 91
10	93	39.289 330 657 370 355 991 128 134 360 7
1000	94	122.321 705 320 204 002 373 196 508 244
40000	95	307.169 772 116 720 722 853 603 759 312

Table 10. $n = 6$ excited-state energy eigenvalues of the sextic anharmonic oscillator as a function of the anharmonicity constant.

β	N	$E_6(3, \beta)$
0.00001	45	13.007 052 770 760 179 284 606 487 1390
10	102	67.698 071 647 819 192 862 730 726 1946
1000	103	211.770 856 103 435 033 789 700 485 021
40000	105	532.031 545 974 229 935 494 398 970 587

Table 11. Convergence rate of successive approximations as a function of the truncation order and the comparison of the results for the ground-state energy of the quartic oscillator.

N	Energy ($\beta = 0.1$)
5	1.065 285 585
10	1.065 285 509 543 811
15	1.065 285 509 543 717 689 3
20	1.065 285 509 543 717 688 857 099
27	1.065 285 509 543 717 688 857 091 628 80
28	1.065 285 509 543 717 688 857 091 628 79
29	1.065 285 509 543 717 688 857 091 628 79
Banerjee	1.065 285 509 543 72
Marziani	1.065 285 509 543 717 688 857 09

Table 12. Convergence rate of successive approximations as a function of the truncation order and the comparison of the results for the ground-state energy of the quartic oscillator.

N	Energy ($\beta = 1$)
5	1.392 359
15	1.392 351 641 530 275
25	1.392 351 641 530 291 855 696
35	1.392 351 641 530 291 855 657 507 652
41	1.392 351 641 530 291 855 657 507 876 63
42	1.392 351 641 530 291 855 657 507 876 54
43	1.392 351 641 530 291 855 657 507 876 58
44	1.392 351 641 530 291 855 657 507 876 60
45	1.392 351 641 530 291 855 657 507 876 59
46	1.392 351 641 530 291 855 657 507 876 61
47	1.392 351 641 530 291 855 657 507 876 61
48	1.392 351 641 530 291 855 657 507 876 61
Banerjee	1.392 351 641 530 29
Marziani	1.392 351 641 53

Table 13. Convergence rate of successive approximations as a function of the truncation order and the comparison of the results for the ground-state energy of the quartic oscillator.

N	Energy ($\beta = 40\,000$)
5	36.275
15	36.274 458 133 739
25	36.274 458 133 736 835 468
35	36.274 458 133 736 835 470 376 378
44	36.274 458 133 736 835 470 376 382 681
45	36.274 458 133 736 835 470 376 382 679
46	36.274 458 133 736 835 470 376 382 6786
47	36.274 458 133 736 835 470 376 382 6785
48	36.274 458 133 736 835 470 376 382 6785
Banerjee	36.274 458 133 736 8
Marziani	—

to overfill the content of the paper with tabular material. As is shown, the acceleration of the convergence is slow relative to the case of the quartic oscillator.

In tables 11-14, some results of Banerjee [20] and Marziani [11] are given explicitly for the comparison of our successive approximations.

5. Convergence discussion and concluding remarks

Let us consider the second-order formally self-adjoint linear differential operator, H:

$$H = -\mathrm{d}^2/\mathrm{d}x^2 + V(x) \tag{5.1}$$

where the potential function, $V(x)$, is analytic, and recall the following quantities which were introduced in § 2:

$$\mu(x) = H\Psi(x)/\Psi(x) \tag{5.2}$$

Table 14. Convergence rate of successive approximations as a function of the truncation order and the comparison of the results for the ground-state energy of the sextic oscillator.

N	Energy ($\beta = 40\,000$)
40	16.211 718 264 749 243 826
50	16.211 718 264 749 243 619 150
60	16.211 718 264 749 243 619 248 486
65	16.211 718 264 749 243 619 248 518
70	16.211 718 264 749 243 619 248 517 588
75	16.211 718 264 749 243 619 248 517 553
80	16.211 718 264 749 243 619 248 517 5559
85	16.211 718 264 749 243 619 248 517 5559
Banerjee	16.211 718 264 749 2
Marziani	—

$$\{D^k\Psi(x)\}_{x=x_0} = 0 \qquad k = 1, 2, \ldots, N \tag{5.3}$$

$$\{D^k H\Psi(x)\}_{x=x_0} = 0 \qquad k = 1, 2, \ldots, N \tag{5.4}$$

$$\mu(x) = \mu(x_0) + \mathrm{O}((x - x_0)^{N+1}). \tag{5.5}$$

Differentiating $H^2\Psi(x)$ we find that

$$D^k H^2\Psi(x) = -D^{k+2}H\Psi(x) + \sum_{j=0}^{k} \binom{k}{j} [D^{k-j}V(x)][D^j H\Psi(x)] \tag{5.6}$$

which implies

$$\{D^k H^2\Psi(x)\}_{x=x_0} = 0 \qquad k = 1, 2, \ldots, N-2. \tag{5.7}$$

In general, we obtain the relation

$$\{D^k H^{m+1}\Psi(x)\}_{x=x_0} = 0 \qquad k = 1, 2, \ldots, N-2m. \tag{5.8}$$

If we now define the more general ratio

$$\mu_N^{(j)}(x) = H^{j+1}\Psi_N(x)/H^j\Psi_N(x) \qquad H^0 \equiv 1 \tag{5.9}$$

from which it follows that

$$\mu_N^{(j)}(x) = \mu_N^{(j)}(x_0) + \mathrm{O}((x - x_0)^{N+1-2j}) \tag{5.10}$$

where N denotes the order of the Wronskian approach. This means that the functional $\mu_N^{(j)}$ is almost constant in an appropriate neighbourhood of the point where $x = x_0$; in other words, it is flattened around x_0. However, the capability of flattening decreases as j increases.

Since the Wronskian approach imposes only conditions about the closedness of Ψ_N, $\Psi_N \in \mathscr{D}(\mathscr{H})$, and of $H\Psi_N$, $H\Psi_N \in \mathscr{D}(\mathscr{H})$, then for $j > 1$ $\mu_N^{(j)}$ may go to infinity at the boundary points of the interval if an operator more general than (5.1) is under consideration. This adversely affects the flattening capability of the method. However, in a sufficiently small vicinity of the point at $x = x_0$, the desired flattening property of $\mu_N^{(j)}$ can be expected. The range of this vicinity depends completely on the structure of the basis functions and the Hamiltonian.

On the other hand, Ψ_N can be written as a linear combination of the true eigenfunctions since it is contained in the domain of the operator; that is,

$$\Psi_N(x) = \sum_{k=0}^{\infty} a_k^{(N)} F_k(x) + R_N(x) \tag{5.11}$$

where F_k stands for the kth true eigenfunction in an increasing eigenvalue ordering of eigenpairs. The existence of a residual function, R_N, permits us to isolate the expansion in terms of F_k from the divergent nature which may appear under the action of various powers of H to Ψ_N. Furthermore, it is assumed that the derivatives of R_N up to the Nth order vanish in the vicinity of the point, x_0. Therefore, the infinite sum in (5.11) may be assumed to globally converge under the action of H^M, where $2M$ is the nearest integer number to N. It is evident that $H^M F_k = \lambda_k^M F_k$. So the self-adjointness and the positive definiteness of H imply

$$a_k^{(N)} = b_k^{(N)} / \lambda_k^M \qquad \{b_k^{(N)}\} \in l_2 \tag{5.12}$$

where l_2 denotes the space of all infinite sequences of $b_k^{(N)}$ for which

$$\left(\sum_{k=0}^{\infty} |b_k^{(N)}|^2 \right)^{1/2} < \infty \tag{5.13}$$

since

$$\{a_k^{(N)}\} \in l_2 \qquad \iota_k^{(N)} \lambda_k^M\} \in l_2. \tag{5.14}$$

Therefore

$$\Psi_N(x) = a_0^{(N)} F_0(x) + \lambda_0^{-M} \sum_{k=1}^{\infty} b_k^{(N)} (\lambda_0/\lambda_k)^M F_k(x) + R_N(x) \tag{5.15}$$

is obtained. Since

$$(\lambda_0/\lambda_k) < 1 \tag{5.16}$$

taking the limit of (5.15) as $N \to \infty$ we have

$$\Psi_\infty(x) = a_0^{(N)} F_0(x) + R_\infty(x). \tag{5.17}$$

Because of the local character of R_∞, which vanishes around x_0, we may write

$$\lim_{N \to \infty} \Psi_N(x) \propto F_0(x) \qquad x \in [x_0 - \delta, x_0 + \delta] \tag{5.18}$$

for sufficiently small values of δ. This property holds only if the coefficients, $a_k^{(N)}$, remain bounded when N tends to infinity. The boundedness of $a_k^{(N)}$ can be shown if we know that the true eigenfunctions have convergent expansions in terms of the selected basis functions, $\{\phi_j\}$. The existence of $R_N(x)$ has no bad influence on these discussions. However, we can even get rid of it by imposing closedness conditions under certain powers of H at the boundary points of the interval.

For generalised anharmonic oscillators, there is no such residual function due to the exponential factor in the structure of the basis functions. Therefore, as a conclusion, we suggest that $\Psi_N(x)$ converges to a ground-state eigenfunction, $F_0(x)$, if the basis functions are properly chosen. The convergence of the excited modes, on the other hand, seems to be provable by using certain properties of the matrix algebra. We shall not, however, deal with this subject in this paper. The convergence of $\Psi_N(x)$ to $F_0(x)$ implies that the most accurate values can be obtained for the ground states. Actually,

it is apparent from numerical results presented in § 4 that the same accuracy as those of the ground states could be obtained for higher modes by increasing the order of the Wronskian approach.

The transformed Hamiltonian (3.13) has three singular points located at $\xi = 0, 1$ and infinity. The irregular singularity at infinity and the additional singular point at $\xi = -1$, for even m, are out of the ξ interval. However, they may influence the convergence of the method. The singularity at $\xi = 0$ is irregular and is taken care of by the exponential factor in the basis functions. The regular singular point $\xi = 1$, from the transformation (3.9), is the image of the origin of the x interval. As a result of these remarks a Frobenius series expansion for the solution of the problem at $x_0 = 0$ or, equivalently, $\xi_0 = 1$ converges in an open unit ball centred at $\xi = 1$. However, if the calculation point x_0 differs from zero then ξ_0 is smaller than one and the corresponding expansion at this point has a convergence radius which is less than unity. If ξ_0 is very close to zero, i.e. when $x_0 \to \infty$, a dramatic slowing down of convergence is expected due to the irregularity of the point at $\xi = 0$. Since the Wronskian approach is a pointwise approximation, such discussions are of considerable importance, hence we use $\xi_0 = 1$ as a calculation point at which the Frobenius expansion has a maximum radius of convergence. Although they are not quoted here, numerical results obtained for various values of ξ show that there is a notable loss of convergence.

On the other hand, any possible extra singularity in the pontential, for example a jump discontinuity, creates additional difficulties. This, of course, changes the convergence character of the exact eigenfunctions. To take care of this kind of problem multipoint expansions and their matching are needed. However, we are not going to consider such problems and assume analyticity of $V(x)$ everywhere as previously stated.

Another interesting aspect in general anharmonic oscillators is the selection of the flexible parameter, α. Even though it looks as if this kind of selection of α is valid for the nearly harmonic regime of the anharmonicity constant, numerical evaluations show that α is very effective in the entire range of β.

Consequently, the Wronskian approach yields very encouraging numerical results. The most important advantage is its simplicity. Further detailed investigation of the method to complete the proof of convergence, in the sense of functional analytical concepts, and to generalise to the multivariable case is under consideration.

References

[1] Taşeli H and Demiralp M 1987 *Theor. Chim. Acta* **71** 315-25
[2] Demiralp M, Baykara N A and Taşeli H 1988 *Theor. Chim. Acta* **74** 39-54
[3] Kato T 1966 *Perturbation Theory for Linear Operators* (Berlin: Springer)
[4] Bartlett J H 1937 *Phys. Rev.* **51** 661-9
[5] Bartlett J H 1955 *Phys. Rev.* **98** 1067-75
[6] Frost A A, Kellogg R E and Curtis E C 1960 *Rev. Mod. Phys.* **32** 313-7
[7] Demiralp M 1986 *Int. J. Quantum Chem.* **29** 221-7
[8] Reed M and Simon B 1978 *Methods of Modern Mathematical Physics* vol IV (New York: Academic)
[9] Bender C 1982 *Int. J. Quantum Chem.* **21** 93-104
[10] Simon B 1982 *Int. J. Quantum Chem.* **21** 3-25
[11] Marziani M F 1984 *J. Phys. A: Math. Gen.* **17** 547-57
[12] Bazley N and Fox D 1961 *Phys. Rev.* **124** 483-92
[13] Reid C 1965 *J. Chem. Phys.* **43** 186-9
[14] Graffi S and Grecchi V 1973 *Phys. Rev.* D **8** 3487-92
[15] Burrows B L and Core P W 1984 *J. Phys. A: Math. Gen.* **17** 559-67

[16] Demiralp M 1983 *J. Math. Phys.* **24** 101-6
[17] Arı N and Demiralp M 1983 *Bull. Istanbul Tech. Univ.* **36** 345-59
[18] Arı N and Demiralp M 1985 *J. Math. Phys.* **26** 1179-86
[19] Biswas S N, Datta K, Saxena R P, Srivasta P K and Varma V S 1973 *J. Math. Phys.* **14** 1190-5
[20] Banerjee K 1978 *Proc. R. Soc.* A **364** 265-75
[21] Banerjee K, Bhatnagar S P, Choudhry V and Kanwal S S 1978 *Proc. R. Soc.* A **360** 575-86
[22] Halpern F R 1973 *J. Math. Phys.* **14** 219-27
[23] Press H W, Flannery B P, Teukolsky S A and Vetterling W T 1986 *Numerical Recipes* (Cambridge: Cambridge University Press)