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Quantization condition for bound and quasibound states

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Abstract. We discuss a quantization condition for bound and quasibound states of separable quantum-mechanical systems. Results for simple non-trivial models suggest that the quantization condition gives the poles of the scattering matrix except for those coming from virtual states.

1. Introduction

Recently, we showed that the Riccati–Padé method, which had been known to yield accurate eigenvalues and eigenfunctions for bound states of quantum-mechanical models [1–6], also gave accurate Siegert eigenvalues [7, 8]. The most appealing feature of the method is that the same quantization condition applies to both bound and quasibound states. Lacking a sound proof of the validity of the method we have tested it on several examples. However, in spite of the revealing information that they provided, we are still unable to answer some relevant questions concerning its applicability.

The purpose of the present paper is twofold: in the first place we consider models for which we know the exact answer, but which are not exactly solvable by means of the Riccati–Padé method. In this way we expect to understand more clearly how the method works, as well as to put to the test the conjecture that the Hankel quantization condition arising from the Riccati–Padé method gives the poles of the scattering matrix associated with bound, resonance and virtual states [9]. In the second place, we investigate whether the Riccati–Padé method applies to tunnel resonances, which are typically broader than the trapped state resonances treated previously [7, 8], but essentially of the same nature [10, 11]. In fact, one can transform a tunnel resonance into a trapped state resonance by continuous deformation of the potential energy barrier [10, 11].

2. The method

Here, we apply the Riccati–Padé method to the second-order differential equation

$$Y''(x) = Q(x)Y(x) \tag{1}$$

where either $0 < x < \infty$ or $-\infty < x < \infty$. We assume that $Q(x)$ can be expanded about $x = 0$ (or about any other conveniently chosen point) in any of the following three forms:

Case A

$$Q(x) = \sum_{j=-2}^{\infty} Q_j x^j \qquad 0 < x < \infty \tag{2}$$

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Case B

$$Q(x) = \sum_{j=0}^{\infty} Q_j x^{2j} \qquad -\infty < x < \infty \tag{3}$$

Case C

$$Q(x) = \sum_{j=0}^{\infty} Q_j x^{j} \qquad -\infty < x < \infty \tag{4}$$

which, for convenience, we treat separately.

The Riccati–Padé method is based on the regularized logarithmic derivative of the solution $Y(x)$,

$$f(x) = \frac{s}{x} - \frac{Y'(x)}{Y(x)} \tag{5}$$

where s is chosen to make $f(x)$ non-singular at $x = 0$. This function is a solution of the Riccati equation

$$f' = f^2 - \frac{2s}{x} f + \frac{s(s-1)}{x^2} - Q. \tag{6}$$

In case A we choose s and f_0 such that $s(s-1) = Q_{-2}$ and $2sf_0 = -Q_{-1}$.

Taking into account that $f(x)$ is analytic at $x = 0$, we look for a solution of (6) in the form of a Taylor series, writing

$$f(x) = \sum_{j=0}^{\infty} f_j x^j \tag{7}$$

for cases A and C, and

$$f(x) = \sum_{j=0}^{\infty} f_j x^{2j+1} \tag{8}$$

for case B. One easily obtains the Taylor coefficients f_j from the expansion of the Riccati equation (6).

The Schrödinger equation for one-dimensional and central field models is a particular case of (1) with $Q(x) = V(x) + l(l+1)/x^2 - E$, where $V(x)$ is the potential-energy function, and E is the total energy. In the one-dimensional case $l(l+1) = 0$, whereas in the central-field case $l = 0, 1, \ldots$ is the angular-momentum quantum number and, in both of them, $s = l + 1$. For symmetric one-dimensional potentials $s = 0 (l = -1)$ or $s = 1 (l = 0)$ correspond to even or odd states, respectively.

For the harmonic oscillator, hydrogen atom, and other exactly and quasi exactly solvable models $f(x)$ is a rational function. In the Riccati–Padé method we go a step further and suppose that a Padé approximant [1–8]

$$[M/N](x) = \frac{\sum_{j=0}^{M} a_j x^j}{\sum_{j=0}^{N} b_j x^j} \tag{9}$$

is a reasonable approximation to $f(x)$ for non-trivial problems. The natural expansion variable for a symmetric one-dimensional potential is x^2 and, in such a case, we therefore construct the approximant $x[M/N](x^2)$ [1–8].

In order to determine the energy E (for example, for case A) we require that

$$[M/N](x) = \sum_{j=0}^{M+N+1} f_j x^j + \mathcal{O}(x^{M+N+2}) \tag{10}$$

which one easily rewrites as a set of $M + N + 2$ equations to be satisfied by the same number of unknowns a_j and b_j. There is a non-trivial solution provided that E is a root of the Hankel determinant [1–8]

$$H_D^d(E) = \begin{vmatrix} f_{d+1} & f_{d+2} & \cdots & f_{D+d} \\ f_{d+2} & f_{d+3} & \cdots & f_{D+d+1} \\ & & \ddots & \\ f_{D+d} & f_{D+d+1} & \cdots & f_{2D+d-1} \end{vmatrix} = 0 \tag{11}$$

of dimension $D = N + 1$ and displacement $d = M - N$. The Taylor coefficients f_j, and consequently the Hankel determinants, are polynomial functions of E which is the only unknown.

If the one-dimensional potential is asymmetric there are two unknowns: E and f_0 which we determine by means of two conditions like (11) [2]. A recent improvement in this approach is based on the separate treatment of the even and odd parts of the Taylor expansion (7) [12]. For the sake of clarity, in this paper we restrict ourselves to the determination of only one unknown parameter.

It is worth noticing that the Riccati–Padé method allows for complex rotation of the coordinate because the Taylor expansion for $f(x)$ is by no means restricted to real values of x. Important consequences emerge from this fact. Consider, for example, the Hamiltonian operator

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \tag{12}$$

and rotate the coordinate in the complex plane according to $x = q\mathrm{e}^{\mathrm{i}\theta}$, where both q and θ are real. One obtains

$$\mathrm{e}^{2\mathrm{i}\theta} H = -\frac{\mathrm{d}^2}{\mathrm{d}q^2} + \mathrm{e}^{2\mathrm{i}\theta} V(q\mathrm{e}^{\mathrm{i}\theta}). \tag{13}$$

If $\mathrm{e}^{2\mathrm{i}\theta} V(q\mathrm{e}^{\mathrm{i}\theta})$ is real for some value of θ between 0 and 2π, then both E and $\mathrm{e}^{2\mathrm{i}\theta} E$ may be roots of the same Hankel determinant. That is to say, one may obtain the eigenvalues of more than one problem from the same sequence of Hankel determinants.

In the present investigation we obtain the Hankel determinants analytically by means of a symbolic processor, and calculate their roots numerically with a Newton–Raphson algorithm exploiting the almost unlimited precision provided by the software. In this way, we expect to rule out the possibility of round-off errors. The Hankel determinants are rich in all kinds of roots. We call spurious those that are unstable under change of dimension, and meaningful those that appear to converge as D increases. The latter may be further subdivided into physical and unphysical. Physical sequences of roots give the eigenvalues of the chosen problem. The velocity of convergence of the sequences of roots depends just slightly on d; therefore, unless stated otherwise it must be assumed that $d = 0$.

3. The Airy equation

As a first example we consider the Airy equation

$$Y''(x) = xY(x). \tag{14}$$

This problem is interesting as it resembles the Schrödinger equation for the field operator, which has proved helpful to understand the effect of complex rotation of the coordinate on the spectrum of the Stark effect in hydrogen [13]. Here, the only unknown parameter is $f_0 = -Y'(0)/Y(0)$ and we choose $s = 0$ assuming that $Y(0) \neq 0$.

In table 1 we show that a sequence of real roots of the Hankel determinants converges rapidly towards

$$f(0) = -\frac{\mathrm{Ai}'(0)}{\mathrm{Ai}(0)} = \frac{3^{1/3}\Gamma(2/3)}{\Gamma(1/3)}. \tag{15}$$

For this particular value of f_0 the solution of the Airy equation $Y(x) = \mathrm{Ai}(x)$ is square integrable in $(0, \infty)$. The root $f_0 = -\mathrm{Bi}'(0)/\mathrm{Bi}(0)$, which would have led to an unbound solution, does not appear in the Hankel determinants.

Table 1. Sequence of real roots of the Hankel determinants for the Airy equation.

D	Root
2	0.721
3	0.728 91
4	0.729 010
5	0.729 011 12
6	0.729 011 132 8
7	0.729 011 132 945
8	0.729 011 132 947 21
9	0.729 011 132 947 226 8
10	0.729 011 132 947 226 979
11	0.729 011 132 947 226 981 39
12	0.729 011 132 947 226 981 418 4
13	0.729 011 132 947 226 981 418 634
14	0.729 011 132 947 226 981 418 636 24
15	0.729 011 132 947 226 981 418 636 264
16	0.729 011 132 947 226 981 418 636 264 701
Exact	0.729 011 132 947 226 981 418 636 264 700

Table 2 shows a sequence of complex conjugate roots converging towards

$$f(0) = -\frac{\mathrm{Ai}'(0) \pm \mathrm{iBi}'(0)}{\mathrm{Ai}(0) \pm \mathrm{iBi}(0)} = \frac{3^{1/3} \mp 3^{5/6}\mathrm{i}}{1 \pm 3^{1/2}\mathrm{i}} \frac{\Gamma(2/3)}{\Gamma(1/3)} \tag{16}$$

which correspond to purely incoming or outgoing waves.

This example suggests that the Hankel quantization condition determines solutions with an asymptotic exponential behaviour commonly related to poles of the scattering matrix [9, 14]. Notice that nowhere in this application have we exploited the fact that the solutions of (14) can be exactly expressed in terms of Airy functions, except for the interpretation of the results. The Riccati–Padé method does not give the exact values of f_0 for a finite determinant dimension because the logarithmic derivative of $Y(x)$ is not a rational function. However, according to tables 1 and 2 such a representation becomes increasingly accurate as D increases.

4. Exactly solvable potential wells and barriers

The time-independent Schrödinger equation with the symmetric potential

$$V(x) = V_0 \,\mathrm{sech}(x)^2 \tag{17}$$

is exactly solvable for both $V_0 < 0$ (potential well) and $V_0 > 0$ (potential barrier) [15]. In appropriate units it is of the form (1) with $Q(x) = V(x) - E$. Since the exact treatment is

Table 2. Sequences of complex conjugate roots of the Hankel determinants for the Airy equation.

D	Re (f_0)	$\lvert \mathrm{Im}(f_0) \rvert$
2	−0.361	0.62
3	−0.364 45	0.631 25
4	−0.364 505 0	0.631 341
5	−0.364 505 559	0.631 342 15
6	−0.364 505 566 4	0.631 342 160 6
7	−0.364 505 566 473	0.631 342 160 772
8	−0.364 505 566 473 60	0.631 342 160 773 96
9	−0.364 505 566 473 613	0.631 342 160 773 973
10	−0.364 505 566 473 613 490	0.631 342 160 773 973 329
11	−0.364 505 566 473 613 490 70	0.631 342 160 773 973 330 90
12	−0.364 505 566 473 613 490 709 2	0.631 342 160 773 973 330 920 1
13	−0.364 505 566 473 613 490 709 317	0.631 342 160 773 973 330 920 35
14	−0.364 505 566 473 613 490 709 318 1	0.631 342 160 773 973 330 920 35
15	−0.364 505 566 473 613 490 709 318 132 8	0.631 342 160 773 973 330 920 35
16	−0.364 505 566 473 613 490 709 318 132 350	0.631 342 160 773 973 330 920 35
Exact	−0.364 505 566 473 613 490 709 318 132 350	0.631 342 160 773 973 330 920 35

not based on an expansion in the variable x, then the Riccati–Padé method will not give an exact result for a finite value of D.

When $V_0 < 0$ the potential (17) supports at least one bound state with energy $V_0 < E < 0$, and the spectrum is continuous for all $E > 0$. The discrete spectrum is given by the well known expression [15]

$$E_n = -\left(n + \tfrac{1}{2} - \tfrac{1}{2}\sqrt{1 - 4V_0}\right)^2 \qquad n = 0, 1, \ldots < \tfrac{1}{2}\sqrt{1 - 4V_0} - \tfrac{1}{2}. \tag{18}$$

Before proceeding with the treatment of this model, notice that the change of variable $x = \mathrm{i}q$ transforms the Schrödinger equation with the potential (17) into

$$Y''(q) + (V_0 \sec(q)^2 - E)Y(q) = 0. \tag{19}$$

The poles of $\sec(q)^2$ at $-\pi/2$ and $\pi/2$ force the boundary conditions $Y(-\pi/2) = Y(\pi/2) = 0$ which result in the discrete spectrum

$$E_n = -\left(n + \tfrac{1}{2} + \tfrac{1}{2}\sqrt{1 - 4V_0}\right)^2 \qquad n = 0, 1, \ldots. \tag{20}$$

According to the argument given earlier, the Riccati–Padé method should yield the eigenvalues (20) in addition to (18).

Table 3 illustrates the convergence of the method for three eigenvalues with $s = 0$ (even solutions) when $V_0 = -20$. The eigenvalue $E = -25$ follows from (20) when $n = 0$ and is below the minimum of the potential well (17). In this case the Hankel quantization condition determines the square integrable solutions of two eigenvalue problems with quite different potential energy functions and boundary conditions.

We now consider a potential barrier of the form (17) ($V_0 > 0$). In this first application of the Riccati–Padé method to barrier penetration, we show that the Hankel quantization condition already gives tunnel resonances. They are broader than trapped state resonances but both are poles of the scattering matrix [10, 11]. Tunnel resonances play a relevant role in the transition-state theory of chemical reactions (as well as in many fields of theoretical physics) and, therefore, there is a great interest in their accurate location [10, 11]. They are associated with solutions of the Schrödinger equation that behave asymptotically as

Table 3. Roots of the Hankel determinants for $V(x) = -20\,\mathrm{sech}(x)^2$.

D	Root 1	Root 2	Root 3
2	−24.9995	−15.9996	
3	−24.999 999 94	−15.999 999 9	−4.02
4	−24.999 999 999 997	−15.999 999 999 98	−3.999
5	−25.000 000 000 000 0	−16.000 000 000 000 0	−3.999 98
6			−3.999 999 7
7			−4.000 000 001
Exact	−25	−16	−4

outgoing waves in all channels. From the asymptotic behaviour of the exact eigenfunctions for the simple two-channel model considered here, [15] one obtains

$$E_n = -4(n \pm \gamma)^2 \qquad -4\left(n \pm \gamma + \tfrac{1}{2}\right)^2 \qquad \gamma = \tfrac{1}{4}(\sqrt{1 - 4V_0} - 1)$$
$$n = 0, 1, 2, \ldots. \tag{21}$$

Table 4 shows sequences of roots of the Hankel determinants for $s = 0$ converging rapidly towards the first three even exact resonances (21) when $V_0 = 20$. The accuracy is similar when $s = 1$. This example shows that the Riccati–Padé method yields the poles of the scattering matrix corresponding to tunnel resonances.

Table 4. Tunnel resonances with $s = 0$ for the potential barrier $20\,\mathrm{sech}(x)^2$.

D	Re (E)	$\lvert\mathrm{Im}(E)\rvert$
2	19.4996	4.444 05
3	19.500 000 08	4.444 097 188
	13.47	20.20
4	19.499 999 999 996	4.444 097 208 66
	13.5001	22.220 52
5	19.499 999 999 999 999 91	4.444 097 208 657 794 1
	13.499 999 7	22.220 486 05
	−0.49	39.999
6	19.500 000 000 000 000 000	4.444 097 208 657 794 425 0
	13.499 999 999	22.220 486 041
	−0.500 04	39.996 88
7	19.500 000 000 000 000 000	4.444 097 208 657 794 425 0
	13.500 000 000 002	22.220 486 043 228 0
	−0.499 999 95	39.996 874 7
8	19.500 000 000 000 000 000	4.444 097 208 657 794 425 0
	13.500 000 000 000 000 3	22.220 486 043 288 973
	−0.499 999 997	39.996 874 88
9	19.500 000 000 000 000 000	4.444 097 208 657 794 425 0
	13.499 999 999 999 999 999 8	22.220 486 043 288 972 125
	−0.500 000 000 002	39.996 874 877 93
Exact	19.5	4.444 097 208 657 794 425 2
	13.5	22.220 486 043 288 972 125
	−0.5	39.996 874 877 920 149 825

5. Gaussian potential

Although the time-independent Schrödinger equation with the Gaussian potential-energy function

$$V(x) = A\exp(\alpha x^2) \tag{22}$$

is not exactly solvable, it nonetheless serves as another illustrative example. Choosing A and α conveniently, we construct different quantum-mechanical models. When $A > 0$ and $\alpha > 0$ we have an infinite well with discrete spectrum for all $E > A$. If $A < 0$ and $\alpha < 0$ the well is finite and the spectrum is discrete for $A < E < 0$ and continuous for all $E > 0$. We obtain a potential barrier when $A > 0$ and $\alpha < 0$. The complex rotation $x = \mathrm{i}q$ transforms the infinite well into the finite well with an overall change of sign that affects the energy. The same change of variable transforms the positive potential barrier into a negative infinite barrier.

For $A = -20$ and $\alpha = -0.1$ the first two sequences of roots converge rapidly towards $E_0 = -18.623\,389\,159\,621$ and $E' = -21.451\,597\,044\,425$ when $s = 0$. The former is the energy of the ground state, but the latter is not an eigenvalue of this model as it lies below the minimum of the potential well. By means of the Riccati–Hill [16] method we verified that $-E'$ is already the ground state of the infinite well with $A = 20$ and $\alpha = 0.1$, in agreement with the complex rotation argument given above. The application of the Riccati–Padé approach to the finite and infinite wells produces exactly the same sequences, except for a change of sign.

Table 5 shows pairs of tunnel resonances for the Gaussian barrier. The imaginary parts satisfy the harmonic relation $\mathrm{Im}(E_1)/\mathrm{Im}(E_0) = 3$ [11] quite accurately for the potential parameters chosen here. The reason for this behaviour is that the ratio $|\alpha/A|$ is sufficiently small in all those cases for the barrier to approach an inverted parabola near the top. We are not aware of previous results for the Gaussian potential barrier which we can compare with ours. We have already verified that the Hankel quantization condition yields sufficiently accurate results for most practical purposes for a class of modified or distorted Eckart potential barriers, to which other approaches have been applied [10, 11]. We do not show those results here because they add no valuable information to the present discussion.

Table 5. Resonances for the Gaussian potential barrier $V(x) = A\exp(\alpha x^2)$.

A	α	s	D	Re (E)	$\lvert\mathrm{Im}(E)\rvert$
20	−0.1	0	5	19.962 493 226 9	1.414 324 909 94
		1		19.812 631 666 3	4.245 396 057
20	−1	0	6	19.624 381 853 2	4.475 895 025 4
		1		18.137 947 130	13.501 547 305

6. Some baffling results

The results above suggest that the Hankel quantization condition yields at least those poles of the scattering matrix associated with bound states and resonances. When the method fails to apply to a given problem we expect to obtain no convergent sequence. In our extensive numerical investigation we have found only two cases for which the Riccati–Padé method appears to give wrong answers. Although we do not understand the reasons for

such atypical behaviour, we discuss those examples here because we believe that they may sometime shed light on the Hankel quantization condition.

Consider the dimensionless Schrödinger equation $Y''(x) = [V(x) - E]Y(x)$ with the exponential potential

$$V(x) = A\exp(\alpha x) \tag{23}$$

and the boundary condition $Y(0) = 0$ (for example, a central-field model with $l = 0$). Notice that the net effect of the change of variables $x = -q$ is the substitution of $-\alpha$ for α. The main reason for choosing this model is that one easily obtains the poles of the scattering matrix from the roots of the Bessel functions $J_\nu(z)$ [17].

When both A and α are negative, the potential (23) may support bound and virtual states. One easily obtains them from the roots of $J_\nu(a) = 0$ in which $\nu = -2\sqrt{-E}/\alpha$ and $a = -2\sqrt{-A}/\alpha$. A straightforward calculation shows that $E_0 = -6.747\,262\,496\,34$, $E_1 = -1.475\,430\,809\,56$, and $E_\nu = -0.705\,423\,127\,1546$ are respectively the first two bound states and the first virtual state when $A = -20.25$ and $\alpha = -1$ [18]. The Hankel determinant H_{12}^0 gives E_0 up to the last digit, whereas for the first excited state we estimate $E_1 = -1.4754$. The accuracy of the Riccati–Padé method is known to decrease with the number of zeros of the solution [1–8], and for the attractive exponential potential this deterioration is particularly noticeable. We could not obtain the virtual state from the determinants H_D^0 and H_D^1, not even by forcing the rational approximation to satisfy the appropriate asymptotic behaviour $f(x \to \infty) = k$. The latter is not surprising because previous use of two-point Padé approximants yielded just slightly better results than the simpler and more economical Hankel quantization condition (11) [6].

When $A > 0$ and $\alpha < 0$ there are only virtual states. Following other authors we choose $A = 1$ and $\alpha = -2/3$ [18, 19]. Table 6 shows two sequences of roots rapidly converging towards values of E suspiciously close, but not exactly equal, to the virtual states obtained from the roots of the Bessel function. What is even more surprising is that the sequences originated in Hankel determinants with $d = 1$ converge towards the same limits, and that forcing the boundary condition of a purely outgoing wave $f(x \to \infty) = -\mathrm{i}k$ does not modify the results in any substantial way. Also notice that one of the virtual states agrees with the exact result more closely than the other. We must therefore conclude that the Riccati–Padé method does not apply to virtual states, and, consequently, that the roots of the Hankel determinants do not give all the poles of the scattering matrix.

As a further test of the Riccati–Padé method we searched for positive roots of the Hankel determinants for the example just discussed. According to the argument above based on the change of variables, those roots should give the eigenvalues supported by $V(x) = \exp(2x/3)$. Table 7 shows that the first two sequences of roots converge rapidly towards the values of E obtained with the Riccati–Hill method [16]. The Riccati–Padé results are more accurate than the Riccati–Hill ones which have been obtained by floating-point arithmetic.

As a final example we choose a symmetric potential which we have already treated before by means of the Riccati–Padé method [7]:

$$V(x) = (x^2 - 2J)\exp(-\lambda x^2) + 2J \qquad J, \lambda > 0, -\infty < x < \infty. \tag{24}$$

Other authors have also selected it to test methods for the calculation of resonances [20–22]. This potential-energy function supports bound states and resonances if the parameters are conveniently chosen. For example, there is only one bound state when $J = 0.8$ and $\lambda = 0.1$ [20, 22]. In a previous application of the Riccati–Padé method, the Hankel quantization condition gave considerably accurate resonances but something surprising happened when

Table 6. Virtual states for the repulsive exponential potential $V(x) = \exp(-2x/3)$.

D	Re (E)	$\lvert \mathrm{Im}(E) \rvert$
4	−0.269	−0.810
	−2.	−1.
6	−0.269 10	−0.808 97
	−1.61	−0.44
8	−0.269 100 5	−0.808 964 87
	−1.616	−0.4335
10	−0.269 100 604	−0.808 964 877
	−1.615 487 9	−0.433 467 4
12	−0.269 100 603 6	−0.808 964 877 86
	−1.615 488 1	−0.433 467 86
Exact	−0.269 092 170 398 522	−0.808 964 705 921 66
	−1.625 261 409 063 81	−0.435 052 262 076 78

Table 7. Eigenvalues for the potential $V(x) = \exp(2x/3)$.

D	E_0	E_1
4	3.679	
6	3.678 346	6.95
8	3.678 347 464	6.932 86
10	3.678 347 460 6	6.932 893 3
12	3.678 347 460 449	6.932 893 130 5
Riccati–Hill	3.678 347 460 4	6.932 893 13

searching for the bound state [7]. The first terms of the sequence of roots appeared to converge towards the bound-state energy reported by other authors [20, 22], but beyond some value of D the Newton–Raphson algorithm became oscillatory. The addition of a small imaginary part to the initial guess removed the oscillations and gave rise to a new sequence that appeared to converge towards a complex value of E. The imaginary part was considerably smaller than the real part but still large enough for the precision of our calculation. Moreover, the agreement between the limits of the sequences for $d = 0$ and $d = 1$ also ruled out the possibility of numerical errors. Table 8 shows the real and complex roots of the Hankel determinants in the neighbourhood of the bound-state eigenvalue for some values of D and d. Commonly, the number of roots in the vicinity of the physical eigenvalue increases with D in such a way that one can rearrange them into more than one sequence converging towards the same limit [1–8]. This is the first time that we find a complex convergent sequence in the neighbourhood of a bound-state eigenvalue. What is even more surprising is that the complex sequence behaves as the primary sequence converging more rapidly and smoothly than the real one, as shown in table 8. Because we were unable to obtain sufficiently accurate results from the Riccati–Hill method for this problem, we calculated the ground-state energy by means of numerical integration. The result shown in table 8 is remarkably close to the real part of the converged complex sequence but the agreement is not complete. At present we are unable to explain this atypical behaviour of the Riccati–Padé method or the meaning of the complex root. From the roots of $\partial H_D^d/\partial E$ we obtain a smoothly convergent real sequence, complex roots begin

to appear at values of $D \geqslant 9$, and the Newton–Raphson algorithm is stable.

Table 8. Roots of the Hankel determinants about the bound state supported by $V(x) = (x^2 - 2J)\exp(-\lambda x^2) + 2J$ when $J = 0.8$ and $\lambda = 0.1$.

D	d	Re (E)	$\lvert \mathrm{Im}(E) \rvert \times 10^8$
2	0	1.0039	
3	0	1.004 080 71	
4	0	1.004 080 695	
5	0	1.004 081 745	
	0	1.004 080 732	0.26
6	0	1.004 080 707	
	0	1.004 080 726	0.293
7	0	1.004 082 751 82	
	0	1.004 080 726 31	0.295
	1	1.004 080 726 301	0.2937
8	0	1.004 080 717	
	0	1.004 080 726 301	0.2931
	1	1.004 080 725 08	
	1	1.004 080 726 301 4	0.293 45
9	0	1.004 080 726 301 57	0.293 46
	1	1.004 080 726 301 53	0.293 48
Numerical integration		1.004 080 724 283 934 430 140	

7. Conclusions

Throughout this paper we have investigated the conjecture that the Riccati–Padé method gives the poles of the scattering matrix. In general, this seems to be the case for bound states and resonances, but the method has failed to give virtual states correctly. It seems that the Hankel quantization condition does not apply to virtual states, although in the case considered above the limits of the sequences of roots lie curiously close to the correct answers.

The occurrence of a convergent sequence of complex roots where one expects discrete spectrum, even when the imaginary part is comparatively small, suggests that the method may occasionally give wrong answers for bound states.

At present we are unable to explain these (in our opinion fascinating) facts or to give a rigorous proof of the validity of the Riccati–Padé method. However, we believe that the present numerical investigation is quite revealing. In particular, the treatment of the Airy equation clearly shows that the Hankel quantization condition already determines square integrable solutions and purely outgoing and incoming waves. It is therefore suitable for the determination of the energies of bound and quasibound states.

A novel contribution of this paper is the promising fact that the Riccati–Padé method applies to tunnel resonances. This finding is not surprising if one takes into account the results of previous investigations showing that the Riccati–Padé method yields broad resonances accurately [7, 8]. Tunnel resonances are a subject of current interest because of their relevant role in the transition-state theory of chemical reactions [10, 11].

In our opinion, it is quite uncommon that a simple and straightforward quantization condition, like the one in the present method, applies to such a wide variety of quite

dissimilar situations. Other approaches tailored for bound states require some kind of modification to be applicable to resonances. In addition, the underlying theory of the Riccati–Padé method is remarkably simple. We believe that these features make the Riccati–Padé method a useful tool (at least as a complement of other approaches), and justify further investigation to find out its range of applicability rigorously.

The two main weaknesses of the Riccati–Padé method in its present form are that the accuracy of the results decrease with the number of nodes of the solution and that the approach described here does not apply to nonseparable problems. In principle, to overcome the former one simply chooses determinants of sufficiently higher dimension. However, in such a case it is unlikely that one can continue analytical calculations that require comparatively huge computer memory, and well designed floating-point algorithms may be preferable. With respect to the second weakness mentioned above, we are presently working on two different ways of extending the method to coupled channel equations. One of them rests on the fact that in this more complex case the logarithmic derivative of the solution also satisfies a matrix Riccati equation. A simpler though possibly more restrictive approach is the treatment of the off-diagonal terms as a perturbation.

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