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**Abstract.** The roots of the Hankel determinant built with the Taylor coefficients of the regularized logarithmic derivative of the eigenfunction give both the bound-state and Siegert eigenvalues (resonances) of separable quantum-mechanical systems. We obtain accurate positions and widths for the resonances of some commonly chosen test examples.

## 1. Introduction

The Riccati–Padé method gives an accurate rational approximation of the regularized logarithmic derivative of the eigenfunction and a sound quantization condition for the eigenvalues [1–7]. The quantization condition states that the roots of a Hankel determinant constructed with the Taylor coefficients of that function are close approximations to the eigenvalues. Extensive numerical calculation has shown that the accuracy increases rapidly with the dimension of the determinant and, consequently, the Riccati–Padé method proves useful in obtaining eigenvalues and eigenfunctions of one-dimensional and central-field models [1–7]. Moreover, from the roots of the Hankel determinants one also obtains either exact or highly accurate weak- and strong-coupling expansions [5, 7].

In this paper we show that the quantization condition given by the Riccati–Padé approach is also valid for Siegert eigenvalues. Siegert states are solutions of the time-independent Schrödinger equation that behave asymptotically as outgoing waves [8]. The real and imaginary parts of the corresponding complex eigenvalues are, respectively, the positions and widths of the scattering resonances in, for example, collisional ionization and detachment processes.

In section 2 we outline the method and derive the quantization condition. In section 3 we calculate the lowest Siegert eigenvalue of an anharmonic oscillator with a negative coupling constant and estimate the velocity of convergence of the method. In section 4 we consider simple one-dimensional and central-field non-polynomial potentials that are commonly chosen to be test examples in the development of methods for the calculation of scattering resonances. Finally, in section 5 we discuss some of the advantages and disadvantages of the Riccati–Padé approach and outline its prospective generalization.

## 2. The Riccati–Padé method

Choosing convenient units, one can reduce the time-independent Schrödinger equation for many simple quantum-mechanical models to

$$\Psi''(x) + \left[ E - V(x) - \frac{l(l+1)}{x^2} \right] \Psi(x) = 0 \tag{1}$$

where $E$ is the energy of the particle, $V(x)$ the potential energy function and, for a one-dimensional motion, $l(l+1) = 0$ and $-\infty < x < \infty$. If $V(x) = V(-x)$ then $l = -1$ and $l = 0$ give rise to the even and odd states respectively. For central-field models $0 \leqslant x < \infty$ and $l = 0, 1, \ldots$ is the angular-momentum quantum number. If, in this case, $V(x)$ behaves as $V_{-2}/x^2$, $V_{-2} > -1/4$, close to the origin, then we add a term to the centrifugal term which results in a real value of $l$ (that is to say we substitute $L(L+1) = l(l+1) + V_{-2}$ for $l(l+1)$ in (1)).

Here, we assume that the potential-energy function of the one-dimensional problem is parity invariant and regular at the origin so that it can be expanded in a Taylor series as

$$V(x) = \sum_{j=0}^{\infty} V_j x^{2j}. \tag{2}$$

In the case of a central-field problem we suppose that

$$V(x) = \sum_{j=-1}^{\infty} V_j x^{j}. \tag{3}$$

The Riccati–Padé method is based on a rational approximation to the regularized logarithmic derivative of the eigenfunction:

$$f(x) = \frac{l+1}{x} - \frac{\Psi'(x)}{\Psi(x)}. \tag{4}$$

which is a solution of the Riccati equation

$$f'(x) = f(x)^2 - \frac{2(l+1)}{x} f(x) - V(x) + E. \tag{5}$$

The term $(l+1)/x$ removes the singularity of $\Psi'/\Psi$ at the origin so that $f(x)$ is regular there and can be expanded in a Taylor series around that point. In the case of a parity-invariant potential we have

$$f(x) = \sum_{j=0}^{\infty} f_j x^{2j+1} \tag{6}$$

with coefficients that follow from the recurrence relation

$$f_n = \frac{1}{2n+2l+3} \left( \sum_{j=0}^{n-1} f_j f_{n-j-1} - V_n + E\delta_{n0} \right) \qquad n = 0, 1, \ldots. \tag{7}$$

Alternatively, for a central-field model the series is of the form

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

and we obtain the coefficients from

$$f_n = \frac{1}{n+2l+3} \left( \sum_{j=0}^{n} f_{j-1} f_{n-j-1} - V_n + E\delta_{n0} \right) \qquad n = -1, 0, 1, \ldots \tag{9}$$

where the sum does not appear when $n = -1$. In both cases the coefficients $f_j$ are polynomial functions of $E$ which is the only unknown parameter of the theory. For an asymmetric one-dimensional potential both the energy and one of the Taylor coefficients remain unknown [3]. For simplicity we do not discuss such a case here.

To take into account its poles and zeros we write $f(x)$ as a Padé approximant $x[N + d/N](x^2)$ $d \geqslant 0$ for a parity-invariant potential, and as $f_{-1} + x[N + d/N](x)$ for a central-field model. Such rational approximations account for the first $2N + d + 1$ coefficients $f_j$ exactly ($2N + d + 2$ if $f_{-1} \neq 0$ in the central-field case). If we also require that they produce the coefficient $f_{2N+d+1}$ then the energy has to be a root of the Hankel determinant

$$H_D^d(E) = \begin{vmatrix} f_{d+1} & f_{d+2} & \cdots & f_{D+d} \\ f_{d+2} & f_{d+3} & \cdots & f_{D+d+1} \\ & & \ddots & \\ f_{D+d} & f_{D+d+1} & \cdots & f_{2D+d-1} \end{vmatrix} = 0 \tag{10}$$

which, for convenience, we express in terms of its dimension $D = N + 1$. Previous calculations of bound-state energies proved that the roots of (10) rapidly converge towards the actual eigenvalues as $D$ increases. The accuracy also depends on $d$ [2], but for brevity we restrict ourselves to $d = 0$ throughout this paper.

One of the surprising features of the Riccati–Padé method is that the derivation of the quantization condition (10) does not, apparently, take into account the asymptotic form of the eigenfunction. Recent numerical calculations have shown that as $D$ increases, the approximate $f(x)$ approaches close to the exact regularized logarithmic derivative of the eigenfunction in an increasingly wider interval about the origin, even though it may not have the appropriate form in the limit $|x| \rightarrow \infty$ [7]. If one is only interested in the energies, then the problem reduces to the calculation of the roots of a polynomial.

## 3. The anharmonic oscillator

As a first illustrative example we consider the anharmonic potential-energy function

$$V(x) = x^2 + \lambda x^4 \tag{11}$$

in one dimension. There are bound states for $\lambda \geqslant 0$ only and a continuum spectrum otherwise. Here, we consider the Siegert states embedded in the continuum for $\lambda < 0$ that have been calculated from the perturbation series by means of numerical integration and through the complex-coordinate method [9–12]. The semi-classical WKB method yields [13]

$$\mathrm{Im}(E^{\mathrm{WKB}}) = \frac{4}{\sqrt{-\pi\lambda}} \exp\left[\frac{2}{3\lambda}\right] \tag{12}$$

for the imaginary part of the lowest resonance considered here. This expression is exact in the limit $\lambda \rightarrow 0^-$.

Since the Hankel determinant is a polynomial with real coefficients, it exhibits pairs of complex-conjugate roots in agreement with the fact that both $E$ and $E^*$ are eigenvalues for real negative values of $\lambda$. However, only the roots with negative imaginary parts describe decaying states or resonances, and through this choice one is taking into account

the asymptotic form of the eigenfunction. For comparison purposes we select $\text{Im}(E) > 0$ for the time being.

The number of roots in the neighbourhood of the actual resonances increases rapidly with the dimension of the determinant. For this reason, it is convenient to begin with determinants of small dimension, which do not have many roots, and increase the dimension by unit steps looking for the roots of $H_D^0$ in the neighbourhood of the roots of $H_{D-1}^0$ previously calculated. This is the simplest way of selecting the best root for every value of $D$.

To quantify the convergence velocity of the Riccati–Padé method we calculate $\log |\{\text{Re}[E^{(D)}] - \text{Re}[E^{(D-1)}]\}/\text{Re}[E^{(D)}]|$ and $\log |\{\text{Im}[E^{(D)}] - \text{Im}[E^{(D-1)}]\}/\text{Im}[E^{(D)}]|$ for increasing values of $D$ and choose two sufficiently different values of $\lambda$ to determine the effect of its magnitude. Figure 1 shows that the resonance position converges slightly faster for $\lambda = -0.05$ than for $\lambda = -1$, and figure 2 reveals that the opposite is true for the resonance width. The reason for the former result is that as $|\lambda|$ decreases the potential (11) becomes increasingly harmonic and the Riccati–Padé method is exact when $\lambda = 0$. To understand the latter, notice that since no root of the Hankel determinant exhibits an essential singularity like that in (12), then the smaller the value of $-\lambda$ the larger the dimension $D$ required for a given accuracy. A concomitant effect is that the imaginary part of a resonance may not appear at low dimensions if $-\lambda$ is small enough (cf figure 2). Except for extremely small values of $-\lambda$, the calculated resonance width is sufficiently accurate for most practical purposes. An important conclusion drawn here is that, apparently, the proper root of the Hankel determinant tends towards the actual resonance as $D$ increases, at least for the values of $\lambda$ considered here. A sufficiently accurate calculation of $\text{Im}(E)$ for values of $\lambda$ closer to zero requires Hankel determinants of a much larger dimension; the application of the method soon becomes impracticable. However, even in such an unfavourable situation one still obtains accurate resonance positions from determinants of moderate dimension.
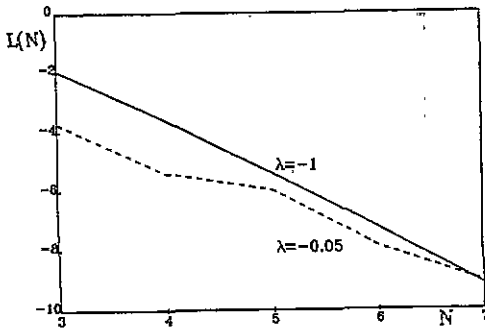


**Figure 1.** Rate of convergence of the Riccati–Padé method expressed as $L(D) = \log |\{\text{Re}[E^{(D)}] - \text{Re}[E^{(D-1)}]\}/\text{Re}[E^{(D)}]|$ for the real part of the lowest Siegert eigenvalue of the anharmonic oscillator with $V(x) = x^2 + \lambda x^4$.
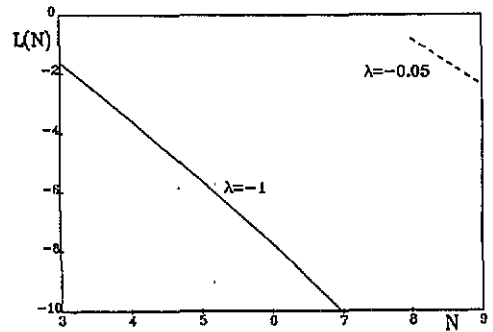
**Figure 2.** Rate of convergence of the Riccati–Padé method expressed as $L(D) = \log |\{\text{Im}[E^{(D)}] - \text{Im}[E^{(D-1)}]\}/\text{Im}[E^{(D)}]|$ for the imaginary part of the lowest Siegert eigenvalue of the anharmonic oscillator with $V(x) = x^2 + \lambda x^4$.

Table 1 shows the lowest resonance for some values of $\lambda$ estimated from the roots of $H_D^0$ for successive values of $D$. For comparison purposes, in the last column we give the ratio [10]

$$\varepsilon = \text{Im}(E)/\text{Im}(E^{\text{WKB}}). \tag{13}$$

**Table 1.** Lowest Siegert eigenvalue of the anharmonic oscillator with the potential $V(x) = x^2 + \lambda x^4$ obtained from determinants with dimension 12.

| $\lambda$ | Re($E$) | Im($E$) | $\varepsilon$ |
|---|---|---|---|
| $-1$ | 0.747 747 833 562 779 45 | 0.609 980 500 214 535 23 | 0.526 454 147 370 324 19 |
| $-0.5$ | 0.722 917 966 899 020 1375 | 0.351 510 988 837 489 5709 | 0.417 828 599 051 747 7311 |
| $-0.2$ | 0.794 881 259 641 709 1472 | 0.089 412 295 066 449 3736 | 0.496 678 611 683 594 393 |
| $-0.1$ | 0.900 672 904 092 015 025 | 0.006 693 280 875 800 130 | 0.736 971 241 810 6441 |
| $-0.05$ | 0.958 233 636 451 927 729 | 0.000 014 564 773 367 893 | 0.891 039 117 674 32 |
| $-0.04$ | 0.967 451 235 236 971 5399 | $0.596 530 736 0513 \times 10^{-6}$ | 0.914 995 864 5171 |
| $-0.02$ | 0.984 427 669 765 255 4008 | $0.510 939 49 \times 10^{-13}$ | 0.959 140 31 |

Present results are more accurate than those obtained with either perturbative or non-perturbative methods [9–12].

By analogy to the case of bound states one expects an expansion of the form

$$E(\lambda) = |\lambda|^{1/3} \sum_{j=0}^{\infty} e_j |\lambda|^{-2j/3} \tag{14}$$

to be valid for resonances when $|\lambda| \to \infty$, where the coefficient $e_0$ is a resonance of $V(x) = -x^4$. Following a procedure that proved to be successful for bound states [5,7], we obtain

$$E(\lambda) \cong |\lambda|^{1/3}[0.530 181 045 242 091 450$$
$$- 0.918 300 507 569 275 964i + (0.181 011 324 + 0.313 520 811i)|\lambda|^{-2/3}$$
$$+ 0.034 510 263|\lambda|^{-4/3}] \tag{15}$$

for the lowest resonance. To the best of our knowledge this expansion has not been reported before. In figure 3 we compare this approximate expansion with the converged roots of the Hankel determinants. The accuracy of the calculated resonances for $\lambda = -5, -10$ and $-100$ is similar to that for $\lambda = -1$. For clarity in figure 3 we have chosen Im($E$) < 0.

## 4. Other simple models

The anharmonic potential-energy function just considered is a polynomial of sufficiently small degree so that the Hankel determinants take all of its terms completely into account. In order to know the effect of a truncation of the Taylor expansion of the potential-energy function on the calculated resonances we concentrate on non-polynomial examples. The first example is the one-dimensional model potential

$$V(x) = (x^2 - 2J) \exp(-\lambda x^2) + 2J \qquad J, \lambda > 0 \tag{16}$$

selected in numerical tests of the complex-coordinate method because the Schrödinger equation exhibits pre-dissociating resonances, analogous to those encountered in diatomic molecules [14, 15]. Table 2 shows the bound state and the two lowest resonances for $J = 0.8$ and $\lambda = 0.1$. Based only on a convergence criterion, present results are more accurate than those obtained by the complex-coordinate method within either the Rayleigh–Ritz variational method, the Numerov algorithm or Milne's complex energy quantization condition [14–16].
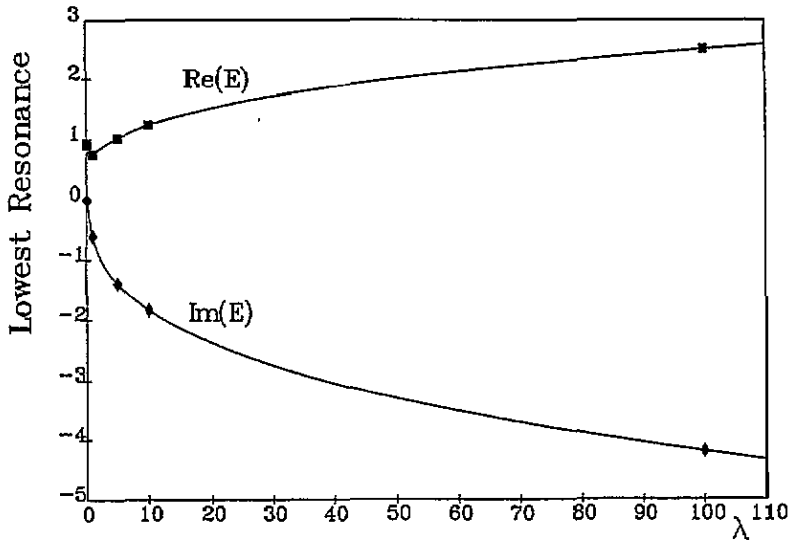
**Figure 3.** Large-$\lambda$ expansion for the lowest resonance supported by $V(x) = x^2 - \lambda x^4$ (full line) compared with the real (squares) and imaginary (diamonds) parts of the converged roots of the Hankel determinants.

**Table 2.** Lowest bound-state energy and resonances of the one-dimensional model with potential-energy function $V(x) = (x^2 - 2J) \exp(-\lambda x^2) + 2J$ for $J = 0.8$ and $\lambda = 0.1$ from a determinant of dimension 11.

| $l$ | $E$ |
|---|---|
| $-1$ | $1.004\,080\,720$ |
| $0$ | $2.841\,941\,891\,429 - 0.000\,116\,530\,562\mathrm{i}$ |
| $-1$ | $4.254\,394\,1551 - 0.030\,894\,6255\mathrm{i}$ |

Our second example is a quantum-mechanical model with the central-field potential

$$V(x) = 2V_0 x^2 \exp(-\lambda x) \qquad x \geqslant 0, \ V_0, \lambda > 0 \tag{17}$$

which has proved suitable for numerical tests of methods developed for the calculation of scattering resonances in auto-ionizing processes such as collisional ionization and detachment [16–22]. Although the convergence of the method is considerably slower for this example, our estimate of the lowest $s$-wave scattering resonance $E = 6.852\,780 - 0.025\,549\mathrm{i}$ ($D = 15$) for $V_0 = 7.5$ and $\lambda = 1$, agrees with those obtained by other approaches [16–22].

In the case of the repulsive potential

$$V(x) = V_0 \exp(-\lambda x) \qquad x \geqslant 0, \ V_0, \lambda > 0 \tag{18}$$

we obtain more than one acceptable root for some values of $D$, even when following the stepwise procedure outlined before. In addition, determinants of different dimension exhibit common roots which makes a judicious choice even more difficult. Our estimates $E_0 = -2.421\,905\,43 - 7.280\,683\,90\mathrm{i}$ and $E_1 = -14.539\,393 - 3.901\,2108\mathrm{i}$ for $V_0 = 9$ and $\lambda = 2$ are slightly different from the results obtained by means of an analytical treatment and using a matching technique combined with complex rotation [22, 23].

The results obtained in this section suggest that the truncation of the Taylor expansion for the potential-energy function does not seriously affect the rate of convergence of the method.

## 5. Further comments and conclusions

Present results clearly support the assumption that the roots of the Hankel determinant, constructed with the Taylor coefficients of the regularized logarithmic derivative of the eigenfunction, give the resonances or Siegert eigenvalues of the system in addition to the bound-state energies. A practical advantage of the Riccati–Padé method is that the roots of the Hankel determinant converge rapidly towards the actual eigenvalues so that our results may, in some cases, be more accurate than those obtained by means of the well-established methods and, in addition, we can easily improve our results by increasing the dimension of the Hankel determinant. Moreover, the Riccati–Padé method is suitable for the application of computer algebra which enables one to obtain analytical expressions for the Hankel determinant and its derivative with respect to the energy. In this way, one easily calculates the roots by means of the Newton–Raphson method, or any other algorithm, with the almost unlimited precision provided by most symbolic processors. In addition to this, analytical expressions for the Hankel determinants facilitate the derivation of power-series expansions such as (14) that would be difficult to obtain otherwise.

The Riccati–Padé method also gives accurate eigenfunctions in a coordinate interval wide enough for the calculation of matrix elements [7]. Such a calculation has to be carried out numerically, and the fact that $f(x)$ does not exhibit the correct asymptotic behaviour is not a hindrance because one stops the numerical integration when $|\Psi(x)|$ is sufficiently small.

One disadvantage of the present approach is that the dimension of the Hankel determinant needed to obtain a given precision increases rapidly with the number of nodes of the eigenfunction. This fact makes the calculation of excited bound-state energies and resonances labelled by large quantum numbers difficult. The application of supersymmetric quantum mechanics partly overcomes this undesirable feature [4].

Another difficulty, already discussed, is the occurrence of many roots in the Hankel determinants. For clarity, we classify the roots into physical and unphysical, and the latter are further classified into spurious and meaningful. Physical roots converge towards the eigenvalues of the chosen problem. One may arrange them in different sequences but it is convenient just to select the best one as indicated before. Spurious roots are those that do not appear to belong to any convergent sequence and, therefore, they are easily singled out. Finally, roots that form convergent sequences with limits that one recognizes as eigenvalues of a different problem from the one chosen are called unphysical meaningful roots. Since the present method is based on the Taylor expansion of the logarithmic derivative of the eigenfunction, it is valid for complex values of the coordinate and, consequently, may apply to a set of models obtained by rotation of the coordinate in the complex plane. Consider the simple model given by $H = -d^2/dz^2 + z^4$ as an illustrative example. When $z = x$ we obtain the pure quartic oscillator; however, when $z = x\exp(i\pi/2)$ we have $H = -(-d^2/dx^2 - x^4)$. For this reason, together with the fact that there is no explicit selection of the asymptotic form of the eigenfunctions, a Hankel determinant for the pure quartic oscillator also exhibits the complex resonances of $H = -d^2/dx^2 - x^4$ times minus unity. A similar situation is encountered in the other models considered above.

It is easy to single out the actual bound states of a problem from the many roots of a Hankel determinant because their approximate location is predictable. Some of the resonances, however, pose a somewhat more difficult problem. For example, in the case of the potential-energy function (17) we also found a sequence of roots rapidly converging towards $E = -11.669\,628\,5625 - 4.380\,265\,522i$. Although the resonances of that model with negative real parts have been investigated [16], the resonance indicated has not been

obtained before and it is not easy to decide whether it corresponds to that potential or to another related by complex rotation of the coordinates. When looking for a more accurate bound-state energy supported by the potential (16), we found that the Newton–Raphson algorithm oscillated in a suspicious way and so we tried a complex starting point; as a result we obtained $E = 1.004\,080\,726\,301\,57 - 0.293\,47 \times 10^{-8}\text{i}$. To verify if this resonance close to the bound state is just a product of the particular Hankel determinants considered, we calculated the roots of a sequence of determinants $H_D^1$ obtaining exactly the same result. An accurate and careful independent calculation is necessary to establish the existence of a complex pole of the scattering matrix in a region where one expects only bound states. Such an eigenvalue would be as difficult to interpret as the resonances with negative real parts supported by the potential-energy function (17) [16].

It follows from the discussion above that the Riccati–Padé method should be applied with great care to the calculation of resonances. However, we deem it to be a useful alternative procedure to verify and even to improve the results obtained from other approaches.

At present, it is not clear to us how to construct the rational approximation to the logarithmic derivative of the eigenfunction for non-separable problems. One possibility is to abandon the quantization condition (10) and minimize the variance of the local energy $H\Psi/\Psi$, $H$ being the Hamiltonian operator, over a set of conveniently chosen coordinate values [24]. One may write the trial function $\Psi$ as $\exp(-F)$, where $F$ is a rational function with adjustable coefficients to be determined according to the criterion just mentioned. This course of action is suggested by the fact that the local energy for simple one-dimensional models proves to be remarkably constant on large intervals of the coordinate when one uses the Riccati–Padé method in the usual way [7]. A second approach is based on a rational approximation to the solution of the matrix Riccati equation [25]. This procedure leads to Hankel determinants of a much larger dimension than those treated here and exhibits the additional disadvantage that the rate of convergence may have a strong dependence on the basis used in the matrix representation of the Schrödinger equation. We are presently investigating such alternative approaches.

## Acknowledgments

## References

[1]   Fernández F M, Frydman G I and Castro E A 1989 *J. Phys. A: Math. Gen.* **22** 641
[2]   Fernández F M, Ma Q and Tipping R H 1989 *Phys. Rev.* A **39** 1605
[3]   Fernández F M, Ma Q and Tipping R H 1989 *Phys. Rev.* A **40** 6149
[4]   Fernández F M, Ma Q, DeSmet D J and Tipping R H 1989 *Can. J. Phys.* **67** 931
[5]   Fernández F M 1992 *Phys. Lett.* **166A** 173
[6]   Fernández F M, Guardiola R and Znojil M 1993 *Phys. Rev.* A **48** 4170
[7]   Fernández F M and Guardiola R 1993 *J. Phys. A: Math. Gen.* **26** 7169
[8]   Siegert A J F 1939 *Phys. Rev.* **56** 750
[9]   Drummond J E 1981 *J. Phys. A: Math. Gen.* **14** 1651
[10]  Karrlein R and Kleinert H 1994 *Phys. Lett.* **187A** 133
[11]  Drummond J E 1982 *J. Phys. A: Math. Gen.* **15** 2321
[12]  Moiseyev N 1982 *Mol. Phys.* **47** 585

[13]  Bender C M and Wu T T 1973 *Phys. Rev.* D **7** 1620
[14]  Moiseyev N, Certain P R and Weinhold F 1978 *Mol. Phys.* **36** 1613
[15]  Atabek O, Lefebvre R and Requena A 1980 *Mol. Phys.* **40** 1107
[16]  Korsch H J, Laurent H and Möhlenkamp R 1982 *J. Phys. B: At. Mol. Phys.* **15** 1
[17]  Bain R A, Bardsley J N, Junker B R and Sukumar C V 1974 *J. Phys. B: At. Mol. Phys.* **7** 2189
[18]  Gazdy B 1976 *J. Phys. A: Math. Gen.* **9** L39
[19]  Isaacson A D, McCurdy C W and Miller W H 1978 *Chem. Phys.* **34** 311
[20]  Korsch H J, Laurent H and Möhlenkamp R 1981 *Mol. Phys.* **43** 1441
[21]  Meyer H-D and Walter O 1982 *J. Phys. B: At. Mol. Phys.* **15** 3647
[22]  Atabek O, Lefebvre R and Jacon M 1982 *J. Phys. B: At. Mol. Phys.* **15** 2689
[23]  Lefebvre R 1984 *Resonances in Electron–Molecule Scattering, Van der Waals Complexes, and Reactive Chemical Dynamics* ed D G Truhlar (Washington, DC: American Chemical Society)
[24]  Frost A A 1942 *J. Chem. Phys.* **10** 240
[25]  Johnson B R 1973 *J. Comput. Phys.* **13** 445