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Milne's differential equation and numerical solutions of the Schrödinger equation I. Bound-state energies for singleand double-minimum potentials

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Abstract. Milne's approach to the numerical solution of the Schrödinger equation via a non-linear differential equation and the quantisation of a quantum action is investigated in detail. An accurate and efficient computational method is presented which allows a rapid second-order convergence onto a desired eigenenergy E_n . Numerical sample calculations demonstrate the efficiency of the method, which has special advantages for accurate calculations of high quantum states. The present method can be easily extended to the calculation of quasi-bound levels at resonance (complex-valued) energies.

1. Introduction

The non-linear differential equation[†]

$$w''(x) + k^{2}(x)w(x) = \frac{1}{w^{3}(x)}$$
(1)

has the interesting property, that a *single* solution w(x) of (1) can generate the *general* solution of the well known linear differential equation

$$u''(x) + k^{2}(x)u(x) = 0$$
⁽²⁾

by means of

$$u(x) = cw(x)\sin\left(\int^{x} w^{-2}(x') \, \mathrm{d}x' - b\right)$$
(3)

where c and b are arbitrary constants.

On the other hand it is possible to write the general solution of (1) in terms of a fundamental set of solutions $u_1(x)$ and $u_2(x)$ of (2)

$$w(x) = (Au_1^2(x) + Bu_2^2(x) + 2Cu_1(x)u_2(x))^{1/2}$$
(4)

where the constants A, B, C are related to the Wronskian W of u_1 and u_2 by $AB - C^2 = W^{-2}$ (Eliezer and Gray 1976, Ray and Read 1979b, 1980). This connection between (1) and (2) has been discovered and rediscovered by various authors. In mathematics a short note by Pinney (1950) should be mentioned. Most work, however,

⁺ Sometimes the right-hand side of equation (1) is written as $a^2/w^3(x)$. The additional factor a^2 can easily be removed, however, by means of the transformation $w(x) \rightarrow a^{1/2}w(x)$ and is omitted in the following.

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can be found in physics, where two main research fields may be distinguished: quantum mechanics and classical dynamics of time-dependent harmonic oscillators.

In quantum mechanics equation (2) appears as the celebrated Schrödinger equation with classical momentum

$$p(x) = [2m(E - V(x))]^{1/2}$$
(5)

 $(k(x) = p(x)/\hbar)$. Here the first reference is—as far as we are aware—an early paper by Milne (1930), who derived equation (1) as a starting point for the determination of the eigenvalues (see § 2 of the present paper), which justifies the name 'Milne's equation' for (1) used in the following. Equation (1) has been derived independently by Wilson (1930) and Young (1931, 1932). The method was used by Wheeler (1937) for the determination of scattering phaseshifts, he called it the 'amplitude-phase method'. Plaskett (1953) and Ballinger and March (1954) applied Milne's approach to an extended Thomas–Fermi model, Hecht and Mayer (1957) discussed Milne's equation in connection with an extension of the WKB expansion, and Peacher and Wills (1967) used it for the numerical calculation of electron scattering factors. Milne's original method for the determination of eigenvalues was used by Ezawa *et al* (1970) for the computation of eigenenergies for the symmetric double-well potential

$$V(x) = -\lambda x^2 + x^4 \qquad (\lambda > 0).$$

More recently Newman and Thorson (1972a, b) developed a method for the numerical solution of the Schrödinger equation, which is closely related to Milne's method (see also Wills 1974, Thorson 1974). Light and co-workers developed semiclassical approximations to bound-state problems (Starkschall and Light 1973, 1974) and the fermion density matrix (Light and Yuan 1973, Yuan and Light 1974, Yuan *et al* 1974) via Milne's equation; the application of Milne's approach to multiple-well potentials as well as scattering problems was also investigated (Lee and Light 1974). These papers contain a number of useful results concerning Milne's method. Very recently Killingbeck (1980) rediscovered Milne's approach (with reference to Young's articles, however) as an alternative to JWKB theory, and tried to stimulate further work on this subject.

In classical mechanics the linear second-order differential equation (2) appears for instance as an equation of motion of a harmonic oscillator with amplitude u and time-dependent 'frequency' k(x), where the independent variable x stands for the time. The study of time-dependent harmonic systems was greatly stimulated by the discovery (Lewis 1967a, b, 1968) of a family of exact dynamical invariants

$$I = \frac{1}{2} \left[u^2 / w^2 + (wu' - w'u)^2 \right]$$
(6)

where the function w is an arbitrary solution of the auxiliary equation (1), i.e. for a given function w the quantity I (the so called Lewis invariant) is a constant of motion. Various derivations and applications of the Lewis invariant have appeared in the literature in connection with Noether's theorem (Lutzky 1978a, b, 1979a, b), time-dependent canonical transformations (Leach 1977, 1978, 1979, 1980), dynamical algebras (Korsch 1979, Kaushal and Korsch 1981) or by means of Ermakov's technique (Ray and Reid 1979a, b, 1980) with reference to an early article by Ermakov (1880). It is interesting that the connection between the study of time-dependent harmonic systems and the Schrödinger equation is only rarely observed in the literature, with the exception of the articles by Bitoun *et al* (1973) and Guyard and Nadeau (1976) as well as two articles by one of the present authors (Korsch 1979, Kaushal and Korsch 1981).

The above list of references to the theory of Lewis invariants is far from being complete, further references can be found in the articles cited above.

There are, of course, other problems in physics where the wave equation (2) appears and where Milne's approach is used. We would like to mention the theory of waveguides in electronics (see, for example, North 1979 and Hashimoto 1979).

In the following we will refer to equation (2) as the Schrödinger equation and discuss the quantum mechanical eigenvalues and eigenfunctions. The translation to other fields in physics, some of which are mentioned above, is obvious, however.

The aim of the present article is twofold; first we discuss Milne's method in more detail than before in the literature. The method turns out to be a powerful tool for the determination of bound-state energies and wavefunctions, both for single-well and double-well potentials, especially for high quantum numbers. The second aim is to set the foundations for a new treatment of complex-valued resonance energies. This will be treated in a further paper.

2. Milne's differential equation and the quantisation condition

Let w(x) be an arbitrary solution of the Milne equation (1) with $k(x) = p(x)/\hbar$ given by equation (5). The general solution of the Schrödinger equation (2) is then given by (3). In the following we concentrate on bound-state problems. In this case it is sufficient to consider real-valued solutions of the Schrödinger equation at real energies. An extension to quasi-bound levels at complex-valued energies will be given in a subsequent paper. We furthermore assume that the interval of interest is $(-\infty, +\infty)$; an extension to $(0, \infty)$ as in the case of the radial Schrödinger equation is straightforward.

At a bound-state energy E_n the wavefunction must satisfy the boundary conditions $\psi(\pm \infty) = 0$. We observe first that w(x) can never be zero on the real axis (there may be zeros, however, in the complex plane). This is evident, for instance, from equation (4), where the radicant is a quadratic form of the independent solutions u_1 and u_2 . The existence of non-trivial zeros of (4) $(u_1(x_0) = u_2(x_0) = 0$ is forbidden, because u_1 and u_2 are independent) is determined by the vanishing of the determinant of the coefficient matrix, which is $AB - C^2 = W^{-2}$ (i.e. the Wronskian of u_1 and u_2) which is also forbidden. In order to satisfy the boundary conditions at infinity, we must therefore have

$$\int_{-\infty}^{+\infty} w^{-2}(x) \, \mathrm{d}x = (n+1)\pi \qquad n = 0, \, 1, \, 2, \, \dots$$
 (7)

which is Milne's quantisation condition for the energy levels E_n . From equations (3) and (7) it is furthermore evident that n represents the number of nodes of the wavefunction. It should be stressed that there are no boundary conditions on w(x), and that the integral also exists for energies different from E_n . The wavefunction (3) is independent of the particular choice of w(x), i.e. the initial conditions $w(x_0)$ and $w'(x_0)$ at some point x_0 . The same is true for the quantisation condition (7). From the computational point of view it is desirable for w(x) to show smooth behaviour. This can be achieved by choosing classical initial conditions for w(x). In order to discuss the behaviour of w(x) in more detail and to obtain more insight into the concept it is useful to consider the semiclassical limit of Milne's equation.

The extreme semiclassical limit $(\hbar \rightarrow 0)$ of Milne's differential equation (1) can be obtained by neglecting w''(x) in equation (1) completely. In this case we obtain

$$w(x) \simeq k(x)^{-1/2}$$
 (8*a*)

or

$$w^{-2}(x) \simeq k(x) \tag{8b}$$

which is valid only in the classically allowed region and breaks down at the classical turning points. In this approximation the wavefunction (3) agrees with the WKB wavefunction in the classically allowed region and the quantisation condition (7) is almost identical with the celebrated WKB quantisation condition

$$\int_{x_1}^{x_2} k(x) \, \mathrm{d}x = (n + \frac{1}{2})\pi \qquad n = 0, 1, 2, \dots$$
(9)

(the missing $\pi/2$ accounts for the contribution from the classically forbidden regions).

For the case of a single turning point at x_T a uniform semiclassical approximation valid on the whole x axis can be obtained by using the differential equation

$$M''(z) + zM(z) = (\pi^2 M^3(z))^{-1}$$
(10)

(Abramowitz and Stegun 1965, equation (10.4.75)) as a comparison equation. A solution of (10) is the modulus of the Airy functions

$$M(z) = [\operatorname{Ai}^{2}(-z) + \operatorname{Bi}^{2}(-z)]^{1/2}.$$
(11)

Mapping the solutions of the differential equation (1) onto the known solutions of (10) one obtains in the usual way (see, for example, Berry and Mount 1972, § 4) the mapping equation

$$S(x) = \int_{x_{\rm T}}^{x} (-k^2(x'))^{1/2} \, \mathrm{d}x' = \frac{2}{3}z^{3/2}$$
(12)

(classically allowed region $x \leq x_T$), and the uniform approximation to w(x) is

$$w(x) \simeq \left(\frac{\pi^2 z(x)}{k^2(x)}\right)^{1/4} M(-z).$$
(13)

Using two single turning point approximations (13) to the w functions and matching the wavefunctions u(x) and their derivatives at the mid-phase point x_m defined by

$$\int_{x_1}^{x_{\rm M}} k(x) \, \mathrm{d}x = \int_{x_{\rm m}}^{x_2} k(x) \, \mathrm{d}x$$

one regains the modified WKB quantisation formula derived by Miller (1968). In addition it should be noted that a two-turning-point uniformisation is possible (see also Lee and Light 1975). Returning to equation (13) and using the asymptotic approximations for the Airy functions one obtains from (13) the primitive semiclassical approximations

$$w(x) \approx \begin{cases} k(x)^{-1/2} & x < x_{\rm T} \\ |k(x)|^{-1/2} \exp(S(x)) & x > x_{\rm T}. \end{cases}$$
(14)

The semiclassical approximation justifies the notions of the quantum momentum (Lee and Light 1974) $P(x) = K(x)\hbar$ with

$$K(x) \coloneqq w^{-2}(x) \tag{15}$$

(also called local momentum (Young 1931)).

It should be noted, however, that the quantum momentum P(x) depends on the initial conditions chosen for the solution of Milne's equation (1). In the following we will always choose classical initial conditions for w(x)

$$w(x_0) = K^{-1/2}(x_0) = k^{-1/2}(x_0)$$

$$w'(x_0) = -\frac{1}{2}K^{-3/2}(x_0) K'(x_0) = 0$$
(16)

where x_0 is the location of the minimum of the potential. Here we assume that the potential has a single minimum. The complications arising for double- or multiple-well potentials are discussed in § 4. The choice (16) leads to a very smooth behaviour of w(x); other choices have also been tried and shown to produce much more complicated behaviour of w(x).

Figure 1 shows an example of the quantum momentum P(x) for a Morse potential

$$V(x) = D[\exp(-\alpha x) - 1]^{2}$$
(17)

with units chosen such that $m = \hbar = 1$ and D = 5, $\alpha = 1/\sqrt{10}$. P(x) was calculated by solving Milne's differential equation (1) numerically (see below), starting with classical



Figure 1. Quantum momentum K(x) and wavefunction u(x) for the Morse oscillator (17) for the eigenstates n = 0 and n = 3. Also shown in the upper panels are the semiclassical approximations (14) in the classically allowed and forbidden regions, which drop down to zero at the classical turning points.

initial conditions (16) at the minimum of the potential and integrating to both sides $(x \to \pm \infty)$. The energy was fixed to the exact bound-state energy $E_n = (n + \frac{1}{2}) - 0.05(n + \frac{1}{2})^2$ for n = 0 and 3. Also shown in figure 1 are the primitive semiclassical approximations (14) in the classically allowed and forbidden regions. The lower panel in figure 1 shows the corresponding wavefunctions (3), which show an oscillating behaviour (n > 0) contrary to the smooth decay of the quantum momentum P(x). This is especially useful for large quantum numbers, where $u_n(x)$ oscillates very rapidly.

The quantisation condition (7)—rewritten in terms of the local momentum K(x)and the quantum number function N(E)—

$$N(E) = \frac{1}{\pi} \int_{-\infty}^{+\infty} K(x) \, \mathrm{d}x = n+1 \qquad n = 0, \, 1, \, 2, \, \dots$$
 (18)

states that at a bound-state energy the area under the K(x) curve is quantised. The close relationship between (18) and the WKB quantisation condition

$$N^{\text{WKB}}(E) = \frac{1}{\pi} \int_{x_1}^{x_2} k(x) \, \mathrm{d}x + \frac{1}{2} = n + 1 \tag{19}$$

should be noted. The term $\frac{1}{2}$ in (19) accounts for the contribution of the classically forbidden regions outside the classical turning points x_1 , x_2 and for the difference between the classical and quantum momentum.

Introducing the quantum action

$$\Phi(x, E) = \int_{x_0}^x K(x') \, \mathrm{d}x'$$
(20)

where x_0 is taken as the location of the potential minimum, and the right-hand and left-hand action integrals

$$N_{\pm}(E) = \frac{1}{\pi} \int_{x_0}^{\pm \infty} K(x') \, \mathrm{d}x'.$$
(21)

Equation (18) reads

$$N(E) = N_{+}(E) - N_{-}(E) = n+1 \qquad n = 0, 1, 2, \dots$$
(22)

and the bound-state wavefunction (3) is

$$u_n(x) = \frac{c_n}{\sqrt{K(x)}} \sin \int_{-\infty}^x K(x') \, \mathrm{d}x'.$$
 (23)

Note again the similarity to the WKB wavefunction.

For numerical applications (see § 3) it will be useful to have explicit expressions for the density of states, i.e. the energy derivative of N(E). Using

$$\frac{\partial \Phi(x, E)}{\partial E} = \frac{2m}{\hbar^2} \int_{x_0}^x \frac{\mathrm{d}x'}{K(x')} \sin^2(\Phi(x', E) - \Phi(x, E)) + \frac{1}{2K(x_0)} \frac{\partial K(x_0)}{\partial E} \sin 2\Phi(x, E)$$
(24)

(Yuan *et al* 1974 appendix A, see also Ezawa *et al* 1970) and the classical initial conditions (16) at x_0 we find

$$\pi \frac{\partial N_{\pm}}{\partial E} = \frac{2m}{\hbar^2} \int_{x_0}^{\pm \infty} \frac{dx'}{K(x')} \sin^2(\Phi(x', E) - \pi N_{\pm}) + \frac{m}{2p^2(x_0)} \sin 2\pi N_{\pm}(E)$$
(25)

and

$$D(E) = \frac{\partial N}{\partial E} = \frac{\partial N_+}{\partial E} - \frac{\partial N_-}{\partial E}.$$
(26)

At a bound state the contributions from the second term in equation (25) vanishes and we have

$$D(E_n) = \frac{2m}{\hbar^2 \pi} \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{K(x)} \sin^2 \int_{-\infty}^{x} K(x') \,\mathrm{d}x' = \frac{2m}{\hbar^2 \pi} c_n^{-2}$$
(27)

i.e. we have a direct relation between the normalisation constant of the wavefunction and the bound-state density

$$c_n^2 = \frac{2m}{\hbar^2 \pi} (D(E_n))^{-1}.$$
 (28)

The semiclassical equivalent of (28) has been derived by Fröman (1978) using phaseintegral methods.

3. Computational method and numerical results

Numerous techniques can be found in the literature for solving the Schrödinger equation. We would like to mention matrix methods, where the boundary value problem of the Schrödinger equation is replaced by a matrix eigenvalue problem by means of expansion into a complete set of basis functions (see, for example, Shore 1973). Other non-iterative methods are the finite differences method (Truhlar 1972) and the finite element method (Malik *et al* 1980). Another type of method is the 'shooting' method, where an initial estimate for E_n is systematically refined. The most prominent and efficient method is the Numerov-Cooley technique integrating in two directions (in and out) with a matching procedure (Cooley 1961, Cashion 1963) or in only one direction (an improvement) (Hajj *et al* 1974, Le Roy 1979, Hajj 1980, Talman 1980). Killingbeck (1977, 1979) integrates also in only one direction and uses a simpler integrating formula.

The present method is of the second type, and similar in spirit to the work of Newman and Thorson (1972a, b); the method is more efficient than the Numerov-Cooley technique, especially for high quantum numbers.

The numerical technique proposed in the present paper is based on the numerical integration of Milne's equation (1) instead of the Schrödinger equation (2). The advantages are as follows: (i) w(x) is slowly varying contrary to u(x), which is especially important for high quantum numbers; (ii) a simple second-order scheme for convergence onto the desired eigenstate is available.

Milne's differential equation is solved numerically starting at the minimum of the potential at x_0 and integrating separately to the right-hand and left-hand sides. The numerical integration of the non-linear differential equation (1) presents no additional difficulties. In our calculations we used a predictor-corrector method suggested by Milne (1933). For convenience a brief description of the method is given in the appendix. It should be noted, however, that the algorithm uses an equidistant set of integration points, which is kept fixed during the calculation, so that the values of the potential required need to be calculated only once. Along with $w(x) = K^{-1/2}(x)$ the integrals (21) for N_+ and N_- are evaluated using Simpson's rule as well as the

derivatives $\partial N_+/\partial E$ and $\partial N_-/\partial E$ via equation (25). For symmetrical potentials we make use of the symmetry relation $N_- = -N_+$. The evaluation of $\partial N_{\pm}/\partial E$ requires the intermediate storage of K(x) and u(x) at the (equidistant) integration points (which are few, however, because of the smoothly varying behaviour of w(x) and K(x)). It should be noted, however, that the integrand in (25) is oscillatory for higher quantum numbers, so that a very accurate integration of (25) would require roughly the same number of integration points as the numerical integration of the Schrödinger equation. The level density $\partial N/\partial E$ is, however, only an auxiliary quantity, which speeds up the iteration procedure to locate a bound-state energy. It is therefore not at all necessary to calculate $\partial N/\partial E$ with the same precision as N(E). In all our calculations the simple trapezoidal rule turned out to be accurate enough. An alternative procedure would be the use of a linear interpolation

$$\partial N/\partial E \simeq (N(E_2) - N(E_1))/(E_2 - E_1)$$

This, however, requires two integrations of the Milne equation per step and was found to be significantly slower. The final computational procedure is straightforward:

(i) Calculate N(E) at various (typically three) trial energies which span roughly the energy region of interest and solve the linear equations

$$E_{\nu}(N_{\nu}) = \alpha_1 N_{\nu} + \alpha_2 N_{\nu}^2 + \alpha_3 N_{\nu}^3 \qquad (\nu = 1, 2, 3)$$

for α_{μ} (the energy is measured from the potential minimum).

(ii) In order to locate a desired bound state E_n a trial energy is calculated from

$$E(N) = \alpha_1 N + \alpha_2 N^2 + \alpha_3 N^3 \tag{29}$$

with N = n + 1.

(iii) For this trial energy \tilde{E}_n Milne's equation is solved and $N(\tilde{E}_n)$ and $\partial N/\partial E$ are calculated followed by a Newton iteration to converge on the desired solution of $N(E_n) = n + 1$. The convergence is of second order. Typically 3-5 iterations are sufficient to calculate an energy eigenvalue with a relative accuracy of 10^{-7} , even for a rather crude initial guess.

The computation scheme proved to be very fast and efficient for all the test calculations which were performed. Some sample calculations will illustrate the method.

Figure 2 shows the quantum number function N(E) as a function of the energy for the harmonic oscillator $(m = \hbar = \omega = 1)$ and the Morse oscillator (17). Also shown are the state densities $D(E) = \partial N/\partial E$. The bound-state energies E_n satisfying $N(E_n) =$ n + 1 are marked. It may be interesting to note that the exact quantum number function N(E) does *not* agree with the semiclassical $N^{WKB}(E)$, (19), in both cases at all energies, in spite of the fact that the semiclassical quantisation (19) gives the correct energy eigenvalues for these potentials, i.e. we have $N(E_n) = N^{WKB}(E_n)$. For other energies N(E) oscillates about $N^{WKB}(E)$.

In order to demonstrate the convergence behaviour of the Milne method in more detail table 1 shows the dependence of the calculated bound-state energy on the number of integration points in comparison with the numbers obtained by the Cooley technique (Cooley 1961). The potential is a Morse potential (17) with the same parameters used by Cooley (1961) as a fit to the H_2^+ potential energy curve. To obtain the results shown in table 1 we used a fixed integration region (-1.3 < x < 1.9) for n = 0 and (-1.3 < x < 2.6) for n = 3 and varying numbers of integration points. It is obvious that the present method gives very precise results using only a few integration points



Figure 2. Quantum number function N(E) (full curves) for the harmonic and Morse oscillators. The bound-state energies E_n satisfying $N(E_n) = n + 1$ are marked. Also shown is the level density $D(E) = \partial N/\partial E$ (broken curves).

Table 1. Dependence of eigenvalues E_0 , E_3 on the number of integration points.

Number of integration points		E_0	E_3		
	Cooley (1961)	This work	Cooley (1961)	This work	
50	-178.810 52	-178.796 58	-126.833 00	-126.278 16	
100	-178.79924	-178.798 48	-126.319 18	-126.28803	
150	-178.798 66	-178.798 53	-126.29441	-126.288 39	
200	-178.798 57	-178.798 54	$-126.290\ 31$	-126.288 43	
Exact	-178.79854		-126.288 44		

even for the ground state, which is the most favourable state for the Cooley method. For higher quantum numbers the present method is even more superior. Table 2 demonstrates for the same potential the fast second-order convergence onto an eigenstate, starting with a rather bad initial guess. Each iteration step is very fast (the calculation of the potential is only required once in the beginning) and we anticipate a significant decrease of computation time compared with Cooley's method.

As a final example we choose the octic oscillator $V(x) = \frac{1}{2}x^8$ $(m = \hbar = 1)$. Figure 3 shows the quantum number function N(E) up to N = 21, the lowest 21 bound-state energies are marked. For this type of potential the N(E) function increases monotonically for $E \to \infty$ with decreasing slope, i.e. increasing level spacing.

Figure 4 demonstrates the relatively small number of integration points for the case n = 19; 99 points were used equidistantly spaced on the x axis with a spacing of $\Delta x = 0.05$. The energy eigenvalue obtained in this way $E_{19} = 133.89335$, is in good agreement with the 'exact' value of $E_{19} = 133.89228$ computed with a smaller step length Δx . The smooth behaviour of K(x) is obvious from figure 4, in sharp contrast to the rapid oscillatory behaviour of the wavefunction $u_{19}(x)$. It should be noted, finally, that the calculated wavefunction (23) is automatically normalised by means of equation (28).

Table 2.	Successive iterates	obtained	with	poor	first	estimates	on	E_0 (200	integration
points).									

	E_0			
Number of iterations	Cooley (1961)	This work		
1	-168.800 00	-168.800 00		
2	-168.45000	-177.78283		
3	-170.70020	-178.763 72		
4	-172.904 49	-178.798 49		
5	-176.702 14	-178.798 54		
6	-178.624 20			
7	-178.797 03			
8	-178.79856			
9	-178.798 57			
Exact		-178.798 54		



Figure 3. As figure 2 for the octic oscillator $V(x) = \frac{1}{2}x^8$ $(m = \hbar = 1)$. Note the different scales for N(E) (full curve) and $\partial N/\partial E$ (broken curve).

A more careful numerical analysis of the dependence of the energy eigenvalues on the steplength Δx showed that the calculated $E_n(\Delta x)$ relates to the true E_n as follows (see Killingbeck 1977, 1979)

$$E_n(\Delta x) \simeq E_n + A(\Delta x)^N \tag{30}$$

for sufficiently small values of Δx . Numerically, it was found that the present method has N = 5 (the Numerov-Cooley method has N = 4 (Killingbeck 1979)). Equation (30) can be used to obtain E_n by extrapolation from the larger step length results, thus avoiding the most time-consuming 'smallest' Δx computation.



Figure 4. Wavefunction $u_n(x)$ for the octic oscillator $V(x) = \frac{1}{2}x^8$ $(m = \hbar = 1)$ and quantum number n = 19. Also shown are the quantum momentum function K(x) (broken curve) and the potential (thin full curve). Note that K(x) is quantised, according to $N(E_n) = \int_{-\infty}^{+\infty} K(x) dx = n + 1$. Note also the smooth behaviour of K(x). The points used in the calculations are marked by dots.

4. Double-minimum potentials

Potentials containing double (or multiple) wells typically present many more difficulties in numerical studies than do single-well potentials (see, for example, Chan and Stelman 1963, Wicke and Harris 1976, Bohmann and Witschel 1979, Talman 1980). In addition there are only a few analytic double-minimum potentials, which can be treated in closed form (Morse and Stückelberg 1931, Manning 1935, Razavy 1980).

The present method, described above, also leads to rather serious difficulties if it is applied naively to double-well potentials—at least for energies below the central maximum of the potential. Nevertheless it has been used successfully for the potential $V(x) = -\lambda x^2 + x^4$ (Ezawa *et al* 1970).

The difficulties are due to the simple fact that one cannot find a quantum momentum function (i.e. initial conditions for the numerical integration of the Milne equation (1)), which is slowly varying on the whole x axis. If one starts the integration with classical initial conditions (16) in one of the wells, the w(x) function is oscillating (and typically small) in the second well. This leads to numerical instabilities of the quantum number function N(E), unless one chooses a very small step length for the numerical integration of (1), but which destroys the appealing simplicity and efficiency of the method. To

demonstrate the behaviour we performed some sample calculations for the harmonic oscillator with a Gaussian barrier

$$V(x) = \frac{1}{2}x^2 + 9\exp(-x^2)$$
(31)

 $(m = \hbar = 1)$, which has been studied by Chan and Stelman (1963). Figure 5 shows the N(E) function for a step length of $\Delta x = 0.002$. The integration was started at the minimum of the potential on the positive x axis and continued separately towards the positive and negative x direction. One observes an unstable behaviour of N(E) below the barrier $V_B = 9$. In the limit $\Delta x \rightarrow 0$ the instabilities are smoothed out and the 'true' N(E) function is obtained. The N(E) function clearly shows the typical appearance of the eigenvalue as pairs, where N(E) suddenly jumps by one. This behaviour closely resembles the energy dependence of scattering phaseshifts at a resonance.



Figure 5. Quantum number function N(E) for a double-well potential (30). N(E) shows numerical instabilities (thin curve), which are only tamed by choosing extremely small step lengths of integration (bold curve). The bound-state energies satisfying $N(E_n) = n + \frac{1}{2}$ are marked by dots. V_B denotes the height of the central potential barrier.

It has thus been demonstrated that the Milne method in its simple form is capable of calculating double-well bound-state energies though the efficiency for single-well potentials is lost. Alternatively one could start the integration procedure at the central maximum of the potential (this was done by Ezawa *et al* 1970). For energies above the threshold one could again use the classical initial conditions (16). This procedure was found to work well for energies considerably above the potential barrier, but for lower energies we again found an oscillatory behaviour of the quantum momentum. This behaviour is demonstrated in figure 6 for the potential (31) and quantum state n = 8, which is the first state above the barrier ($E_8 \approx 10.12 > V_B = 9$). One observes that K(x) agrees with the classical momentum k(x) in a small region at the origin and starts to oscillate. In this calculation the rather small integration step length of $\Delta x = 0.01$ has been used to obtain a converged energy eigenvalue of $E_8 = 10.122$ 34.

A simple and appealing modification of the Milne method, which regains efficiency has been suggested by Lee and Light (1974); it has, however, apparently never been applied practically. In this modification, the integration is started separately from both potential minima, and the wavefunctions (3) are matched at an intermediate point, which can be taken as the location of the central maximum of the potential. This leads to a modification of the quantisation condition. For simplicity we restrict ourselves to symmetric potentials with a maximum at x = 0. Defining

$$\bar{N}(E) = \frac{1}{\pi} \int_{-\infty}^{0} K(x) \, \mathrm{d}x$$
(32)

and

$$\delta(E) = -\frac{1}{\pi} \cot^{-1}(K'(0)/2K^2(0))$$
(33)

we obtain different quantum number functions for symmetric (S) and antisymmetric (A) eigenfunctions

$$N_{\rm S}(E) = \bar{N}(E) + \delta(E)$$

$$N_{\rm A}(E) = \bar{N}(E)$$
(33)

with the quantisation condition

$$N_{S,A}(E) = n+1.$$
 (34)

A similar result can be obtained for non-symmetric potentials (see Lee and Light 1974). In the interval $(-\infty, 0) K(x)$ is slowly varying, as in the case of a single-well potential. The correction term $\delta(E)$ is very small for energies far below the barrier and increases



Figure 6. Classical momentum k(x)(---) and quantum momenta K(x) for the symmetric double-well potential (31) and eigenstate n = 8 ($E_8 \simeq 10.12$, which is just above the potential barrier $V_B = 9$). Two initial conditions for the calculation of K(x) are compared: classical starting conditions (16) at the central maximum $(-\cdot - \cdot)$ and at one of the potential minima (----).



Figure 7. Modified quantum number functions for symmetric (N_S) and antisymmetric (N_A) states of the double-well potential (31). The bound-state energies are marked by dots. The inset shows the rapid increase of $\delta(E) = N_S(E) - N_A(E)$ on an enlarged scale.

		E_n					
	Chan and Sto						
n	20 basis functions	40 basis functions	Present work				
0	3.075 40	3.075 40	3.075 395				
1	3.078 51	3.078 51	3.078 507				
2	5.138 37	5.138 30	5.138 300				
3	5.164 38	5.164 37	5.164 373				
4	6.971 47	6.971 40	6.971 396				
5	7.098 51	7.098 40	7.098 398				
6	8.576 48	8.576 21	8.576 210				
7	8.968 53	8.967 88	8.967 876				
8	10.124 0	10.1223	10.122 34				
9	10.825 5	10.824 2	10.824 22				
10	11.8314	11.8298	11.829 80				
11	12.6964	12.695 5	12.695 54				
12	13.663 2	13.6619	13.661 91				
13	14.5916	14.5897	14.589 72				
14	15.565 0	15.5517	15.551 72				
15	16.521 2	16.504 6	16.504 57				
16		_	17.470 54				
17	<u> </u>		18.435 54				
18	_		19.406 53				
19	_	_	20.378 63				

Table 3. Double-well eigenvalues for the harmonic oscillator with Gaussian barrier (30). The results of the present method are compared with the numbers calculated by Chan and Stelman (1963), who used an expansion into basis functions.

to $\frac{1}{2}$ for $E \to \infty$, with a steep rise in the vicinity of the barrier $E \simeq V_{\rm B}$. Setting l = 2n for symmetric and l = 2n + 1 for antisymmetric states we recover for $E \to \infty$ the single-well quantisation condition $N(E) = 2\overline{N} = l + 1$.

The quantisation condition (33) was solved numerically by the methods described in § 3; the derivative of K'(x) at x = 0 in equation (32) was computed by numerical interpolation. Test calculations for model potentials, which can be solved in closed form (Manning 1935, Razavy 1980) reproduced the exact eigenvalues to any desired accuracy. A sample calculation for the potential (31) is shown in figures 6 and 7. Figure 6 shows the quantum momentum K(x) for the present method (starting at the potential minimum) for the eigenstate n = 8. K(x) is very smooth and closely follows the classical momentum k(x), in contrast to the oscillatory behaviour of K(x) for different initial conditions (starting the integration at the central maximum) as discussed above. The $N_{S,A}(E)$ functions are slowly varying in contrast to N(E) (compare figure 5). The inset of figure 7 shows the correction $\delta(E)$ on an enlarged scale. $\delta(E)$ increases from 0 to 0.5 as the energy passes the barrier V_B . The eigenvalues obtained in this manner are given in table 3 in comparison with the results of Chan and Stelman (1963).

Table 4. Some ground-state (n = 0) eigenvalues for the Hamiltonian $-\Delta + r^2 + r^{-\alpha}$ obtained by Killingbeck (1981) and reproduced exactly by the present Milne method. The bracketed results are those of Detwiler and Klauder (1975).

λ	$\alpha = 4$		$\alpha = 6$	
0.01	3.205 07	(3.205 27)	3.505 45	(3.505 74)
0.005	3.148 35	(3.148 39)	3.422 88	(3.42302)
0.0025	3.106 81	(3.106 70)	3.353 92	(3.353 95)

5. Conclusions

The results presented here demonstrate that the Milne method offers a powerful tool for the calculation of bound-state energies. In addition, it is obvious that the Milne approach leads to rather interesting aspects of semiclassical approximations. Work along these lines is currently proceeding. The most remarkable finding, however, is the fact that the present method can be extended to the calculation of complex-valued resonance energies in a straightforward manner. This will be the topic of a subsequent paper[†].

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⁺ As a further check of our method we have recently rechecked some eigenvalues obtained by Detwiler and Klauder (1975) for the Hamiltonian $-\Delta^2 + r^2 + \lambda r^{-\alpha}$ ($0 < r < \infty$) using Ezawa's program (Ezawa *et al* 1970). Their results have recently been questioned by Killingbeck (1981), who obtained different values. Our Milne method calculation identically reproduced Killingbeck's results, which are given in table 4.

Appendix

Milne's differential equation (1) can be conveniently solved numerically by a predictor– corrector method for the numerical solution of the non-linear second-order differential equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = f(x, y) \tag{A.1}$$

(Milne 1933). For convenience we give a brief description of the numerical techniques which are due to Milne (1933) (for a modern presentation see Lambert (1973) in particular ch 9). We assume equidistant integration points x_i , i = 0, 1, 2, ..., with spacing $\Delta x = x_{i+1} - x_i$. Let us assume that $y_i = y(x_i)$ is already known at j = i - 3, i - 2, i - 1, i. y_{i+1} is then predicted by

$$y_{i+1} = y_i + y_{i-2} - y_{i-3} + (\Delta^2 x/4)(5f_i + 2f_{i-1} + 5f_{i-2})$$
(A.2)

and—after calculation of $f_{i+1} = f(x_{i+1}, y_{i+1})$ —corrected by

$$y_{i+1} = 2y_i - y_{i-1} + (\Delta^2 x/12)(f_{i+1} + 10f_i + f_{i-1})$$
(A.3)

followed by another calculation of f_{i+1} . These equations are then iterated. If more values of y_i are known, it is worthwhile to use the more accurate higher order formulae

$$y_{i+1} = y_i + y_{i-4} - y_{i-5} + (\Delta^2 x/48)(67f_i - 8f_{i-1} + 122f_{i-2} - 8f_{i-3} + 67f_{i-4})$$
(A.4)

for prediction and

$$y_{i+1} = y_i + y_{i-2} - y_{i-3} + (\Delta^2 x/240)(17f_{i+1} + 232f_i + 222f_{i-1} + 232f_{i-2} + 17f_{i-3})$$
(A.5)

for correction instead of equations (A.2) and (A.3).

In order to start the iteration via (A.2) and (A.3) we have to know the initial values. Expanding the solution y(x) of the Milne equation (1)

$$y'' + k^2(x)y = y^{-3}$$
(A.6)

to fifth order about the potential minimum x_0

$$y = \sum_{\nu=0}^{5} \lambda_{\nu} (x - x_{0})^{\nu}$$
 (A.7)

calculating y''(x) and expanding $k^2(x)$ we obtain by comparison of the coefficients (we use classical initial conditions (16))

$$\lambda_{0} = y_{0} = k^{-1/2}(x_{0})$$

$$\lambda_{1} = \lambda_{2} = \lambda_{3} = 0$$

$$\lambda_{4} = \frac{m}{12\hbar^{2}} V''(x_{0})y_{0}$$

$$\lambda_{5} = \frac{m}{60\hbar^{2}} V'''(x_{0})y_{0}.$$
(A.8)

These values are used in (A.7) to calculate y_i at the four initial points $x_i = x_0 + i\Delta x$ for i = -1, 0, 1, 2. We use (A.2), (A.3) until y_i is available at six points, then we switch to the more precise expressions (A.4) and (A.5).

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