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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 $\dagger$

$$
\begin{equation*}
w^{\prime \prime}(x)+k^{2}(x) w(x)=\frac{1}{w^{3}(x)} \tag{1}
\end{equation*}
$$

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

$$
\begin{equation*}
u^{\prime \prime}(x)+k^{2}(x) u(x)=0 \tag{2}
\end{equation*}
$$

by means of

$$
\begin{equation*}
u(x)=c w(x) \sin \left(\int^{x} w^{-2}\left(x^{\prime}\right) \mathrm{d} x^{\prime}-b\right) \tag{3}
\end{equation*}
$$

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)

$$
\begin{equation*}
w(x)=\left(A u_{1}^{2}(x)+B u_{2}^{2}(x)+2 C u_{1}(x) u_{2}(x)\right)^{1 / 2} \tag{4}
\end{equation*}
$$

where the constants $A, B, C$ are related to the Wronskian $W$ of $u_{1}$ and $u_{2}$ by $A B-C^{2}=W^{-2}$ (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,
$\dagger$ 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.
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

$$
\begin{equation*}
p(x)=\left[2 m(E-V(x)]^{1 / 2}\right. \tag{5}
\end{equation*}
$$

$(k(x)=p(x) / \hbar)$. 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 wкв 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

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

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

$$
\begin{equation*}
I=\frac{1}{2}\left[u^{2} / w^{2}+\left(w u^{\prime}-w^{\prime} u\right)^{2}\right] \tag{6}
\end{equation*}
$$

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) $\left(u_{1}\left(x_{0}\right)=u_{2}\left(x_{0}\right)=0\right.$ is forbidden, because $u_{1}$ and $u_{2}$ are independent) is determined by the vanishing of the determinant of the coefficient matrix, which is $A B-C^{2}=W^{-2}$ (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

$$
\begin{equation*}
\int_{-\infty}^{+\infty} w^{-2}(x) \mathrm{d} x=(n+1) \pi \quad n=0,1,2, \ldots \tag{7}
\end{equation*}
$$

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 $w\left(x_{0}\right)$ and $w^{\prime}\left(x_{0}\right)$ 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 $w^{\prime \prime}(x)$ in equation (1) completely. In this case we obtain

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

or

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

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

$$
\begin{equation*}
\int_{x_{1}}^{x_{2}} k(x) \mathrm{d} x=\left(n+\frac{1}{2}\right) \pi \quad \mathrm{n}=0,1,2, \ldots \tag{9}
\end{equation*}
$$

(the missing $\pi / 2$ accounts for the contribution from the classically forbidden regions).
For the case of a single turning point at $x_{\mathrm{T}}$ a uniform semiclassical approximation valid on the whole $x$ axis can be obtained by using the differential equation

$$
\begin{equation*}
M^{\prime \prime}(z)+z M(z)=\left(\pi^{2} M^{3}(z)\right)^{-1} \tag{10}
\end{equation*}
$$

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

$$
\begin{equation*}
M(z)=\left[\mathrm{Ai}^{2}(-z)+\mathrm{Bi}^{2}(-z)\right]^{1 / 2} \tag{11}
\end{equation*}
$$

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

$$
\begin{equation*}
S(x)=\int_{x_{\mathrm{T}}}^{x}\left(-k^{2}\left(x^{\prime}\right)\right)^{1 / 2} \mathrm{~d} x^{\prime}=\frac{2}{3} z^{3 / 2} \tag{12}
\end{equation*}
$$

(classically allowed region $x \leqslant x_{\mathrm{T}}$ ), and the uniform approximation to $w(x)$ is

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

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 $x_{\mathrm{m}}$ defined by

$$
\int_{x_{1}}^{x_{\mathrm{M}}} k(x) \mathrm{d} x=\int_{x_{\mathrm{m}}}^{x_{2}} k(x) \mathrm{d} x
$$

one regains the modified wкв 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

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

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

$$
\begin{equation*}
K(x):=w^{-2}(x) \tag{15}
\end{equation*}
$$

(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 $w(x)$

$$
\begin{align*}
& w\left(x_{0}\right)=K^{-1 / 2}\left(x_{0}\right)=k^{-1 / 2}\left(x_{0}\right) \\
& w^{\prime}\left(x_{0}\right)=-\frac{1}{2} K^{-3 / 2}\left(x_{0}\right) K^{\prime}\left(x_{0}\right)=0 \tag{16}
\end{align*}
$$

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 $\S 4$. 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

$$
\begin{equation*}
V(x)=D[\exp (-\alpha x)-1]^{2} \tag{17}
\end{equation*}
$$

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 $(x \rightarrow \pm \infty)$. The energy was fixed to the exact bound-state energy $E_{n}=$ $\left(n+\frac{1}{2}\right)-0.05\left(n+\frac{1}{2}\right)^{2}$ 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 $N(E)$ -

$$
\begin{equation*}
N(E)=\frac{1}{\pi} \int_{-\infty}^{+\infty} K(x) \mathrm{d} x=n+1 \quad n=0,1,2, \ldots \tag{18}
\end{equation*}
$$

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

$$
\begin{equation*}
N^{\mathrm{WKB}}(E)=\frac{1}{\pi} \int_{x_{1}}^{x_{2}} k(x) \mathrm{d} x+\frac{1}{2}=n+1 \tag{19}
\end{equation*}
$$

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

$$
\begin{equation*}
\Phi(x, E)=\int_{x_{0}}^{x} K\left(x^{\prime}\right) \mathrm{d} x^{\prime} \tag{20}
\end{equation*}
$$

where $x_{0}$ is taken as the location of the potential minimum, and the right-hand and left-hand action integrals

$$
\begin{equation*}
N_{ \pm}(E)=\frac{1}{\pi} \int_{x_{0}}^{ \pm \infty} K\left(x^{\prime}\right) \mathrm{d} x^{\prime} \tag{21}
\end{equation*}
$$

Equation (18) reads

$$
\begin{equation*}
N(E)=N_{+}(E)-N_{-}(E)=n+1 \quad n=0,1,2, \ldots \tag{22}
\end{equation*}
$$

and the bound-state wavefunction (3) is

$$
\begin{equation*}
u_{n}(x)=\frac{c_{n}}{\sqrt{K(x)}} \sin \int_{-\infty}^{x} K\left(x^{\prime}\right) \mathrm{d} x^{\prime} \tag{23}
\end{equation*}
$$

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
$\frac{\partial \Phi(x, E)}{\partial E}=\frac{2 m}{\hbar^{2}} \int_{x_{0}}^{x} \frac{\mathrm{~d} x^{\prime}}{K\left(x^{\prime}\right)} \sin ^{2}\left(\Phi\left(x^{\prime}, E\right)-\Phi(x, E)\right)+\frac{1}{2 K\left(x_{0}\right)} \frac{\partial K\left(x_{0}\right)}{\partial E} \sin 2 \Phi(x, E)$
(Yuan et al 1974 appendix A, see also Ezawa et al 1970) and the classical initial conditions (16) at $x_{0}$ we find
$\pi \frac{\partial N_{ \pm}}{\partial E}=\frac{2 m}{\hbar^{2}} \int_{x_{0}}^{ \pm \infty} \frac{\mathrm{d} x^{\prime}}{K\left(x^{\prime}\right)} \sin ^{2}\left(\Phi\left(x^{\prime}, E\right)-\pi N_{ \pm}\right)+\frac{m}{2 p^{2}\left(x_{0}\right)} \sin 2 \pi N_{ \pm}(E)$
and

$$
\begin{equation*}
D(E)=\frac{\partial N}{\partial E}=\frac{\partial N_{+}}{\partial E}-\frac{\partial N_{-}}{\partial E} . \tag{26}
\end{equation*}
$$

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

$$
\begin{equation*}
D\left(E_{n}\right)=\frac{2 m}{\hbar^{2} \pi} \int_{-\infty}^{+\infty} \frac{\mathrm{d} x}{K(x)} \sin ^{2} \int_{-\infty}^{x} K\left(x^{\prime}\right) \mathrm{d} x^{\prime}=\frac{2 m}{\hbar^{2} \pi} c_{n}^{-2} \tag{27}
\end{equation*}
$$

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

$$
\begin{equation*}
c_{n}^{2}=\frac{2 m}{\hbar^{2} \pi}\left(D\left(E_{n}\right)\right)^{-1} \tag{28}
\end{equation*}
$$

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 NumerovCooley 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

$$
\partial N / \partial E \simeq\left(N\left(E_{2}\right)-N\left(E_{1}\right)\right) /\left(E_{2}-E_{1}\right) .
$$

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

$$
E_{\nu}\left(N_{\nu}\right)=\alpha_{1} N_{\nu}+\alpha_{2} N_{\nu}^{2}+\alpha_{3} N_{\nu}^{3} \quad(\nu=1,2,3)
$$

for $\alpha_{\mu}$ (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

$$
\begin{equation*}
E(N)=\alpha_{1} N+\alpha_{2} N^{2}+\alpha_{3} N^{3} \tag{29}
\end{equation*}
$$

with $N=n+1$.
(iii) For this trial energy $\tilde{E}_{n}$ Milne's equation is solved and $N\left(\tilde{E}_{n}\right)$ and $\partial N / \partial E$ are calculated followed by a Newton iteration to converge on the desired solution of $N\left(E_{n}\right)=n+1$. 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 $N\left(E_{n}\right)=$ $n+1$ are marked. It may be interesting to note that the exact quantum number function $N(E)$ does not agree with the semiclassical $N^{\mathrm{WKB}}(E)$, (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 $N\left(E_{n}\right)=N^{\mathrm{WKB}}\left(E_{n}\right)$. For other energies $N(E)$ oscillates about $N^{\mathrm{wKB}}(E)$.

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 $\mathrm{H}_{2}^{+}$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 $N\left(E_{n}\right)=n+1$ 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 <br> integration <br> points | $E_{0}$ |  |  | $E_{3}$ |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | Cooley (1961) | This work |  | Cooley (1961) | This work |
| 50 | -178.81052 | -178.79658 |  | -126.83300 | -126.27816 |
| 100 | -178.79924 | -178.79848 |  | -126.31918 | -126.28803 |
| 150 | -178.79866 | -178.79853 |  | -126.29441 | -126.28839 |
| 200 | -178.79857 | -178.79854 |  | -126.29031 | -126.28843 |
| Exact | -178.79854 |  | -126.28844 |  |  |

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 $E \rightarrow \infty$ 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 $\Delta x$. 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 <br> iterations | Cooley (1961) | This work |
| 1 | -168.80000 | -168.80000 |
| 2 | -168.45000 | -177.78283 |
| 3 | -170.70020 | -178.76372 |
| 4 | -172.90449 | -178.79849 |
| 5 | -176.70214 | -178.79854 |
| 6 | -178.62420 |  |
| 7 | -178.79703 |  |
| 8 | -178.79856 |  |
| 9 | -178.79857 |  |
| Exact |  |  |



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 $\Delta x$ showed that the calculated $E_{n}(\Delta x)$ relates to the true $E_{n}$ as follows (see Killingbeck 1977, 1979)

$$
\begin{equation*}
E_{n}(\Delta x) \approx E_{n}+A(\Delta x)^{N} \tag{30}
\end{equation*}
$$

for sufficiently small values of $\Delta x$. 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' $\Delta x$ 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 $N\left(E_{n}\right)=$ $\int_{-\infty}^{+\infty} K(x) \mathrm{d} x=n+1$. 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

$$
\begin{equation*}
V(x)=\frac{1}{2} x^{2}+9 \exp \left(-x^{2}\right) \tag{31}
\end{equation*}
$$

( $m=\hbar=1$ ), 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 $V_{\mathrm{B}}=9$. 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 $N\left(E_{n}\right)=n+\frac{1}{2}$ are marked by dots. $V_{\mathrm{B}}$ 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 ( $E_{8} \simeq 10.12>V_{B}=9$ ). 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 $E_{8}=10.12234$.

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

$$
\begin{equation*}
\bar{N}(E)=\frac{1}{\pi} \int_{-\infty}^{0} K(x) \mathrm{d} x \tag{32}
\end{equation*}
$$

and

$$
\begin{equation*}
\delta(E)=-\frac{1}{\pi} \cot ^{-1}\left(K^{\prime}(0) / 2 K^{2}(0)\right) \tag{33}
\end{equation*}
$$

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

$$
\begin{align*}
& N_{\mathrm{S}}(E)=\bar{N}(E)+\delta(E) \\
& N_{\mathrm{A}}(E)=\bar{N}(E) \tag{33}
\end{align*}
$$

with the quantisation condition

$$
\begin{equation*}
N_{\mathrm{S}, \mathrm{~A}}(E)=n+1 . \tag{34}
\end{equation*}
$$

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 $V_{\mathrm{B}}=9$ ). Two initial conditions for the calculation of $K(x)$ are compared: classical starting conditions (16) at the central maximum (-.-.) and at one of the potential minima (-).


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

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.

|  | $E_{n}$ |  |  |
| ---: | :--- | :--- | :--- |
|  | Chan and Stelman (1963) |  |  |
| $n$ | 20 basis functions | 40 basis functions | Present work |
| 0 | 3.07540 | 3.07540 | 3.075395 |
| 1 | 3.07851 | 3.07851 | 3.078507 |
| 2 | 5.13837 | 5.13830 | 5.138300 |
| 3 | 5.16438 | 5.16437 | 5.164373 |
| 4 | 6.97147 | 6.97140 | 6.971396 |
| 5 | 7.09851 | 7.09840 | 7.098398 |
| 6 | 8.57648 | 8.57621 | 8.576210 |
| 7 | 8.96853 | 8.96788 | 8.967876 |
| 8 | 10.1240 | 10.1223 | 10.12234 |
| 9 | 10.8255 | 10.8242 | 10.82422 |
| 10 | 11.8314 | 11.8298 | 11.82980 |
| 11 | 12.6964 | 12.6955 | 12.69554 |
| 12 | 13.6632 | 13.6619 | 13.66191 |
| 13 | 14.5916 | 14.5897 | 14.58972 |
| 14 | 15.5650 | 15.5517 | 15.55172 |
| 15 | 16.5212 | 16.5046 | 16.50457 |
| 16 | - | - | 17.47054 |
| 17 | - | - | 18.43554 |
| 18 | - | - | 19.40653 |
| 19 | - |  | 20.37863 |

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

The quantisation condition (33) was solved numerically by the methods described in § 3; the derivative of $K^{\prime}(x)$ 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 $N_{\mathrm{s}, \mathrm{A}}(E)$ 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 $V_{\mathrm{B}}$. 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).

| $\lambda$ | $\alpha=4$ |  | $\alpha=6$ |  |
| :--- | :--- | :--- | :--- | :--- |
| 0.01 | 3.20507 | $(3.20527)$ | 3.50545 | $(3.50574)$ |
| 0.005 | 3.14835 | $(3.14839)$ | 3.42288 | $(3.42302)$ |
| 0.0025 | 3.10681 | $(3.10670)$ | 3.35392 | $(3.35395)$ |

## 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 papert.

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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 predictorcorrector method for the numerical solution of the non-linear second-order differential equation

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

(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 $x_{i}, i=0,1,2, \ldots$, with spacing $\Delta x=x_{i+1}-x_{i}$. Let us assume that $y_{j}=y\left(x_{j}\right)$ is already known at $j=i-3, i-2$, $i-1, i . y_{i+1}$ is then predicted by

$$
\begin{equation*}
y_{i+1}=y_{i}+y_{i-2}-y_{i-3}+\left(\Delta^{2} x / 4\right)\left(5 f_{i}+2 f_{i-1}+5 f_{i-2}\right) \tag{A.2}
\end{equation*}
$$

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

$$
\begin{equation*}
y_{i+1}=2 y_{i}-y_{i-1}+\left(\Delta^{2} x / 12\right)\left(f_{i+1}+10 f_{i}+f_{i-1}\right) \tag{A.3}
\end{equation*}
$$

followed by another calculation of $f_{i+1}$. These equations are then iterated. If more values of $y_{j}$ are known, it is worthwhile to use the more accurate higher order formulae
$y_{i+1}=y_{i}+y_{i-4}-y_{i-5}+\left(\Delta^{2} x / 48\right)\left(67 f_{i}-8 f_{i-1}+122 f_{i-2}-8 f_{i-3}+67 f_{i-4}\right)$
for prediction and
$y_{i+1}=y_{i}+y_{i-2}-y_{i-3}+\left(\Delta^{2} x / 240\right)\left(17 f_{i+1}+232 f_{i}+222 f_{i-1}+232 f_{i-2}+17 f_{i-3}\right)$
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)

$$
\begin{equation*}
y^{\prime \prime}+k^{2}(x) y=y^{-3} \tag{A.6}
\end{equation*}
$$

to fifth order about the potential minimum $x_{0}$

$$
\begin{equation*}
y=\sum_{\nu=0}^{5} \lambda_{\nu}\left(x-x_{0}\right)^{\nu} \tag{A.7}
\end{equation*}
$$

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

$$
\begin{align*}
& \lambda_{0}=y_{0}=k^{-1 / 2}\left(x_{0}\right) \\
& \lambda_{1}=\lambda_{2}=\lambda_{3}=0  \tag{A.8}\\
& \lambda_{4}=\frac{m}{12 \hbar^{2}} V^{\prime \prime}\left(x_{0}\right) y_{0} \quad \lambda_{5}=\frac{m}{60 \hbar^{2}} V^{\prime \prime \prime}\left(x_{0}\right) y_{0}
\end{align*}
$$

These values are used in (A.7) to calculate $y_{i}$ at the four initial points $x_{i}=x_{0}+\mathrm{i} \Delta x$ 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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