# The Schrodinger equation with an anharmonic oscillator potential



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# The Schrödinger equation with an anharmonic oscillator potential

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**Abstract.** The Liouville–Green uniform asymptotic method is used to obtain approximate eigenvalues and eigenfunctions of the one-dimensional Schrödinger equation with an anharmonic oscillator potential. The term neglected in the basic differential equation, in accordance with the method, is studied in some detail.

## 1. Introduction

In a recent paper (Stephenson 1977), the Liouville–Green technique was used to obtain the eigenvalues of the Schrödinger equation with a radial Gaussian potential. Recent work on the anharmonic oscillator (e.g. Gillespie 1976, Fung *et al* 1978, Banerjee *et al* 1978) has led to computation and comparison of the eigenvalues of the Schrödinger equation. In view of the fact that the Liouville–Green technique and other so-called semi-classical methods are not as widely applied as they might be (Berry and Mount 1972), and of the importance of the anharmonic oscillator potential in nuclear structure, quantum chemistry and quark confinement, we now use the same method for this potential. The eigenvalues obtained are compared with those found by direct methods.

## 2. The basic transformation

Setting $2m = \hbar = 1$, the one-dimensional Schrödinger equation with an anharmonic oscillator potential $V = x^2 + x^4$ is

$$\frac{d^2\psi}{dx^2} = (-E + x^2 + x^4)\psi, \tag{2.1}$$

where $E$ is the energy and the boundary conditions are $\psi(\infty) = \psi(-\infty) = 0$. We make the Liouville–Green transformation

$$x = x(\xi), \qquad \psi(x) = (\xi')^{-1/2} G(\xi), \tag{2.2}$$

where primes denote differentiation with respect to $x$, so that (2.1) becomes

$$d^2G/d\xi^2 = (P(x)/\xi'^2 + \Delta(x))G, \tag{2.3}$$

where

$$P(x) = x^4 + x^2 - E \tag{2.4}$$

  

and

$$\Delta(x) = \xi'''/2\xi'^3 - 3\xi''^2/4\xi'^4. \tag{2.5}$$

When $E$ is positive, $P(x)$ has two zeros $x = \pm x_0$ where

$$x_0 = \{[-1 + (1+4E)^{1/2}]/2\}^{1/2}, \tag{2.6}$$

these being the classical turning points.

The Liouville–Green technique consists in choosing $\xi(x)$ so that $\Delta(x)$ is a small bounded function and (2.3), with $\Delta(x)$ neglected, is soluble in terms of known functions. Two ways of achieving this will be presented. First, since (2.1) has two turning points, we may try to choose $\xi(x)$ so that, after neglecting $\Delta(x)$, (2.3) becomes the standard two-turning-point equation, namely the Weber equation

$$\mathrm{d}^2G/\mathrm{d}\xi^2 = (\xi^2/4 - \lambda)G, \tag{2.7}$$

the solutions of which are the parabolic cylinder functions, where $\lambda$ is a parameter. Alternatively, since $P(x)$ depends only on $x^2$, the wavefunctions $\psi(x)$ will be either even or odd functions and we can consider the problem for $x \geqslant 0$, applying the additional boundary condition that either $\psi(0) = 0$ or $\psi'(0) = 0$. In this case, since $P(x)$ has only one zero for $x \geqslant 0$, we may try to choose $\xi(x)$ so that (2.3) becomes the Airy equation

$$\mathrm{d}^2G/\mathrm{d}\xi^2 = (\xi - a)G, \tag{2.8}$$

after neglecting $\Delta(x)$, where $a$ is a parameter to be determined from the boundary conditions.

Both approaches lead to approximate eigenvalues and eigenfunctions (Olver 1974).

## 3. The Weber equation method

With the choice

$$\xi'^2(\xi^2/4 - \lambda) = P(x), \tag{3.1}$$

(2.3) becomes the Weber equation (2.7), if we neglect $\Delta(x)$. Assuming for the moment that this is justified, we find by integration of (3.1) that for $x \geqslant x_0$,

$$\tfrac{1}{2}\xi(\xi^2 - 4\lambda)^{1/2} - 2\lambda \ln|\xi + (\xi^2 - 4\lambda)^{1/2}| + 2\lambda \ln(2\sqrt{\lambda}) = 2\int_{x_0}^{x} (P(t))^{1/2}\,\mathrm{d}t, \tag{3.2}$$

while between the turning points

$$\frac{\xi}{2}(4\lambda - \xi^2)^{1/2} + 2\lambda \sin^{-1}\left(\frac{\xi}{2\sqrt{\lambda}}\right) = 2\int_0^x (-P(t))^{1/2}\,\mathrm{d}t. \tag{3.3}$$

The constants of integration have been chosen so that $\xi = 0$ when $x = 0$ and $\xi = \pm 2\sqrt{\lambda}$ correspond to $x = \pm x_0$. Putting $x = x_0$ in (3.3) we obtain

$$\lambda\pi = 2\int_0^{x_0} (E - t^2 - t^4)^{1/2}\,\mathrm{d}t. \tag{3.4}$$

The boundary conditions $\psi(\infty)=\psi(-\infty)=0$ correspond to $G(\infty)=G(-\infty)=0$ and bounded solutions of the Weber equation satisfying these conditions exist only if

$$\lambda = n+\tfrac{1}{2}, \tag{3.5}$$

where $n=0, 1, 2, \ldots$.

Substituting (3.5) into (3.4) gives

$$\frac{\pi}{2}(n+\tfrac{1}{2}) = \int_0^{x_0} (E-t^2-t^4)^{1/2}\,\mathrm{d}t, \tag{3.6}$$

which is the Bohr–Sommerfeld quantisation formula, on noticing that

$$\int_0^{x_0} (E-t^2-t^4)^{1/2}\,\mathrm{d}t = \tfrac{1}{2}\int_{-x_0}^{x_0} (E-t^2-t^4)^{1/2}\,\mathrm{d}t. \tag{3.7}$$

Using (3.6), the eigenvalues have been computed and in table 1 are compared with accurate values calculated by Banerjee *et al* (1978) using scaled bases. The two sets of values are in close agreement, the accuracy increasing with increasing $n$.

**Table 1.** Eigenvalues computed using equation (3.6) are compared with accurate values calculated by Banerjee *et al* (1978) using scaled bases.

| $n$ | Eigenvalue | Accurate eigenvalue | Approximate percentage error |
|---|---|---|---|
| 0 | 1·2508 | 1·3924 | 10·17 |
| 1 | 4·5926 | 4·6488 | 1·21 |
| 2 | 8·6130 | 8·6550 | 0·49 |
| 3 | 13·1231 | 13·1568 | 0·26 |
| 4 | 18·0290 | 18·0576 | 0·16 |
| 5 | 23·2725 | 23·2974 | 0·11 |
| 6 | 28·8130 | 28·8353 | 0·077 |
| 7 | 34·6206 | 34·6408 | 0·058 |
| 8 | 40·6717 | 40·6904 | 0·046 |
| 9 | 46·9477 | 46·9650 | 0·037 |
| 10 | 53·4329 | 53·4491 | 0·03 |
| 20 | 127·6076 | 127·6178 | 0·008 |
| 30 | 214·7721 | 214·7797 | 0·0035 |
| 40 | 311·8254 | 311·8315 | 0·002 |
| 50 | 417·0512 | 417·0563 | 0·0012 |
| 100 | 1035·5422 | 1035·5442 | 0·0002 |

We now examine the neglected term $\Delta(x)$. From (2.4) and (3.1) we have

$$\xi' = [(-E+x^2+x^4)/(\xi^2/4-\lambda)]^{1/2}, \tag{3.8}$$

from which $\xi''$ and $\xi'''$ can be calculated in terms of $x$ and $\xi$ and, using (2.5), $\Delta(x)$ can be written out explicitly as

$$\Delta(x) = \frac{(3\xi^2+8\lambda)}{64(\xi^2/4-\lambda)^2} - (\xi^2/4-\lambda)\frac{[2E+(12E+3)x^2+6x^4+8x^6]}{4(-E+x^2+x^4)^3}. \tag{3.9}$$

At the turning points, although both terms in (3.9) diverge, we can show that $\Delta(x)$ tends to a finite limit, as follows:

Using L'Hôpital's rule in (3.8), we have

$$L_1 = \lim_{x\to x_0} \xi' = \left(\frac{2x_0+4x_0^3}{\sqrt{\lambda}}\right)^{1/3}. \tag{3.10}$$

By differentiation of (3.8) and use of L'Hôpital's rule, we find

$$L_2 = \lim_{x\to x_0} \xi'' = \frac{(4+24x_0^2-L_1^4)}{10L_1^2\sqrt{\lambda}} \tag{3.11}$$

and

$$L_3 = \lim_{x\to x_0} \xi''' = \frac{(48x_0\sqrt{\lambda}-24\lambda L_1L_2^2-9\sqrt{\lambda}L_1^3L_2)}{14\lambda L_1^2}. \tag{3.12}$$

$L_1, L_2$ and $L_3$ are non-zero and finite so that by (2.5), $\Delta(x)$ tends to a finite limit given by

$$\lim_{x\to x_0} \Delta(x) = \frac{L_3}{2L_1^3} - \frac{3}{4}\frac{L_2^2}{L_1^4}. \tag{3.13}$$

The values of $\Delta(x)$ have been computed by first finding $\xi$ for a given $x$ from (3.2) or (3.3) and then substituting in (3.9), with the value at the turning point given by (3.13). The results are shown in figures 1 and 2 for selected values of $n$ and indicate that $\Delta(x)$ attains its absolute maximum at $x = 0$, this value decreasing with increasing $n$, and that $\Delta(x)$ is a small, bounded, slowly varying function.

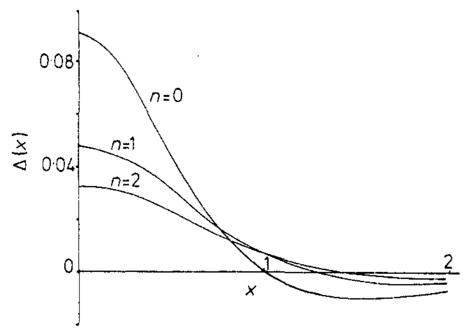


**Figure 1.** $\Delta(x)$ against $x$, for $n = 0, 1, 2$.

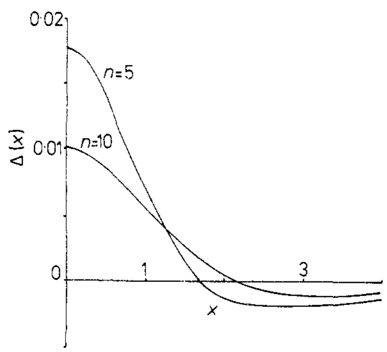


**Figure 2.** $\Delta(x)$ against $x$, for $n = 5, 10$.

## 4. The Airy equation method

Here we consider $x \geqslant 0$, and with the choice

$$\xi'^2(\xi - a) = P(x), \tag{4.1}$$

(2.3) becomes the Airy equation (2.8) on neglecting $\Delta(x)$. We then find by integration of (4.1) that for $x \geqslant x_0$,

$$\tfrac{2}{3}(\xi-a)^{3/2} = \int_{x_0}^{x} (P(t))^{1/2}\,dt, \tag{4.2}$$

the constant of integration being chosen so that $x = x_0$ corresponds to $\xi = a$. For $0 \leqslant x \leqslant x_0$, we have

$$\tfrac{2}{3}a^{3/2} - \tfrac{2}{3}(a-\xi)^{3/2} = \int_0^x (-P(t))^{1/2}\,\mathrm{d}t, \tag{4.3}$$

where $x = 0$ corresponds to $\xi = 0$. Substituting $x = x_0$ into (4.3), we obtain

$$\tfrac{2}{3}a^{3/2} = \int_0^{x_0} (E - t^2 - t^4)^{1/2}\,\mathrm{d}t. \tag{4.4}$$

The required solution of (2.8) is the Airy function $\mathrm{Ai}(\xi - a)$, since this satisfies the boundary condition $G(\infty) = 0$. We can now find the parameter $a$ from the additional condition that either $G'(0) = 0$ or $G(0) = 0$ corresponding to even and odd wavefunctions respectively, since this condition implies that either $\mathrm{Ai}'(-a) = 0$ or $\mathrm{Ai}(-a) = 0$. Hence $-a$ is the position of either a turning point or a zero of the Airy function Ai. The values of $a$ obtained from Abramowitz and Stegun (1964, p 478) were used to compute the eigenvalues using (4.4). The results are shown in table 2 and compare favourably with accurate values.

**Table 2.** Values of $a$ obtained from Abramowitz and Stegun (1964) were used to compute the eigenvalues using equation (4.4).

| $n$ | $a$ from $\mathrm{Ai}'(-a) = 0$ | $a$ from $\mathrm{Ai}(-a) = 0$ | Eigenvalue | Accurate eigenvalue |
|---|---|---|---|---|
| 0 | 1·01 879 | | 1·0706 | 1·3924 |
| 1 | | 2·33 811 | 4·6573 | 4·6488 |
| 2 | 3·24 820 | | 8·5471 | 8·6550 |
| 3 | | 4·08 795 | 13·1605 | 13·1568 |
| 4 | 4·82 010 | | 17·9849 | 18·0576 |
| 5 | | 5·52 056 | 23·3000 | 23·2974 |
| 6 | 6·16 331 | | 28·7788 | 28·8353 |
| 7 | | 6·78 671 | 34·6428 | 34·6408 |
| 8 | 7·37 218 | | 40·6433 | 40·6904 |
| 9 | | 7·94 413 | 46·9666 | 46·9650 |
| 10 | 8·48 849 | | 53·4084 | 53·4491 |
| 11 | | 9·02 265 | 60·1310 | 60·1295 |
| 12 | 9·53 545 | | 66·9589 | 66·9950 |
| 13 | | 10·04 017 | 74·0371 | 74·0359 |
| 14 | 10·52 766 | | 81·2108 | 81·2435 |
| 15 | | 11·00 852 | 88·6115 | 88·6103 |
| 16 | 11·47 506 | | 96·0998 | 96·1296 |
| 17 | | 11·93 602 | 103·7966 | 103·7953 |
| 18 | 12·38 479 | | 111·5743 | 111·6018 |
| 19 | | 12·82 878 | 119·5454 | 119·5442 |

The connection between (3.6) and (4.4) can be seen by noting that the leading order term in the asymptotic expansion of $a$ is

$$a \sim [\tfrac{3}{4}\pi(n + \tfrac{1}{2})]^{2/3} \tag{4.5}$$

where $n = 0, 1, 2, \ldots$ (see Abramowitz and Stegun p 450).

The neglected term $\Delta(x)$ in this case is given by

$$\Delta(x)=\frac{5}{16(\xi-a)^2}-(\xi-a)\frac{[2E+(12E+3)x^2+6x^4+8x^6]}{4(-E+x^2+x^4)^3}, \tag{4.6}$$

and we can again show that $\Delta(x)$ tends to a finite limit at the turning point $x=x_0$. Using the results

$$K_1=\lim_{x\to x_0}\xi'=(2x_0+4x_0^3)^{1/3}, \tag{4.7}$$

$$K_2=\lim_{x\to x_0}\xi''=\frac{(2+12x_0^2)}{5K_1^2}, \tag{4.8}$$

$$K_3=\lim_{x\to x_0}\xi'''=\frac{12}{7K_1^2}(2x_0-K_1K_2^2), \tag{4.9}$$

we obtain from (2.5)

$$\lim_{x\to x_0}\Delta(x)=\frac{3}{28K_1^5}(16x_0-15K_1K_2^2). \tag{4.10}$$

The results of computing $\Delta(x)$ for selected values of $a$ are shown in figures 3 and 4.

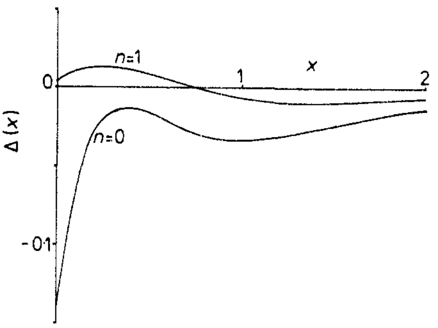


**Figure 3.** $\Delta(x)$ against $x$, for selected values of $a$ $(n=0,1)$.

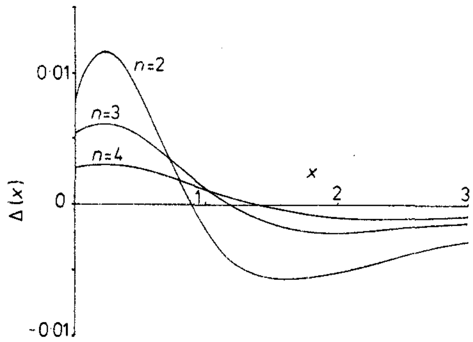


**Figure 4.** $\Delta(x)$ against $x$, for selected values of $a$ $(n=2,3,4)$.

## 5. Discussion

The method presented here depends on the initial choice of $\xi(x)$. Consider for example the Weber equation method. The exact relation between $\xi$ and $x$ is given by

$$(\tfrac{1}{4}\xi^2-\lambda)-\frac{P(x)}{\xi'^2}=\frac{\xi'''}{2\xi'^3}-\frac{3}{4}\frac{\xi''^2}{\xi'^4}, \tag{5.1}$$

and on neglecting the right-hand side, we obtain (3.1). The next approximation would then be

$$(\tfrac{1}{4}\xi^2-\lambda)-P(x)/\xi'^2=\Delta(x(\xi)), \tag{5.2}$$

from which we see that

$$\int_0^{x_0} (-P(x))^{1/2}\,\mathrm{d}x = \int_0^{\xi_0} \{\lambda - \tfrac{1}{4}\xi^2 + \Delta(x(\xi))\}^{1/2}\,\mathrm{d}\xi, \tag{5.3}$$

where $\xi_0$ is given by

$$\lambda - \tfrac{1}{4}\xi_0^2 + \Delta(x(\xi_0)) = 0. \tag{5.4}$$

Except for the case $n = 0$, $\Delta(x)$ is negative at the turning point $x = x_0$ (corresponding to $\xi = 2\sqrt{\lambda}$), so that $\xi_0 < 2\sqrt{\lambda}$. Hence an upper bound for the right-hand side of (5.3) is

$$2\sqrt{\lambda}(\lambda + \Delta(0))^{1/2}, \tag{5.5}$$

which, from (5.3), gives an upper bound for the eigenvalues in this approximation. For upper and lower bounds derived using the WKB approximation, see Birx and Houk 1977.

The approximate eigenfunctions follow from (2.7) or (2.8) and the transformation (2.2).

A wide class of potentials can be treated in a similar manner, for example the interaction of the type $\lambda x^2/(1+gx^2)$ (see Mitra 1978).

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